

## PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

EXXON CHEMICAL LIMITED  
EXXON CHEMICAL TECHNOLOGY CENTRE  
Attn. Bawden, Peter Charles  
P.O. BOX 1  
ABINGDON, OXFORDSHIRE OX13 6BB  
UNITED KINGDOM

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

(PCT Rule 44.1)

2 SEP 1994

FILE 93A007

Date of mailing  
(day/month/year)

31.03.94

DUE

Applicant's or agent's file reference

93A007

FOR FURTHER ACTION See paragraphs 1 and 4 below

International application No.

PCT/EP 94/01301

International filing date  
(day/month/year)

25/04/94

Applicant

EXXON CHEMICAL PATENTS INC. et al.

1. ☒ The applicant is hereby notified that the international search report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

**When?** The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report; however, for more details, see the notes on the accompanying sheet.

**Where?** To the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2; the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Further action(s): The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patenlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl  
Fax: (+31-70) 340-3016

Authorized officer

OF NEGOTIELLI

## NOTES TO FORM PCT/ISA/220

These notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty and of the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT administrative Instructions respectively.

### INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

#### What parts of the international application may be amended?

The claims only.

The description and the drawings may only be amended during international preliminary examination under Chapter II.

#### When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

#### Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

#### How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

#### What documents must/may accompany the amendments?

##### Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confounded with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

### NOTES TO FORM PCT/ISA/220 (continued)

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:  
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; Claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:  
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:  
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or  
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:  
"Claims 1-10 unchanged; claims 11 TO 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

#### "Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings which cannot be amended under Article 19(1).

The statement will be published with the international application and the amended claims.

The statement should be brief, it should not exceed 500 words if in English or if translated into English.

It should not be confounded with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)".

It should not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

#### In what language?

The amendments must be made in the language in which the international application is published. The letter and any statement accompanying the amendments must be in the same language as the international application if that language is English or French; otherwise, it must be in English or French, at the choice of the applicant.

#### Consequence if a demand for international preliminary examination has already been filed?

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

#### Consequence with regard to translation of the international application for entry into the national phase?

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Office, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>93A007</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP 94/01301</b>	International filing date (day/month/year) <b>25/04/94</b>	(Earliest) Priority Date (day/month/year) <b>23/04/93</b>
Applicant <b>EXXON CHEMICAL PATENTS INC. et al.</b>		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ Certain claims were found unsearchable (see Box I).
2. ☐ Unity of invention is lacking (see Box II).
3. ☐ The international application contains disclosure of a nucleotide and/or amino acid sequence listing and the international search was carried out on the basis of the sequence listing
  - ☐ filed with the international application.
  - ☐ furnished by the applicant separately from the international application,
    - ☐ but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
  - ☐ Transcribed by this Authority
4. With regard to the title, ☒ the text is approved as submitted by the applicant.  
☐ the text has been established by this Authority to read as follows:
5. With regard to the abstract,
  - ☒ the text is approved as submitted by the applicant.
  - ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.
6. The figure of the drawings to be published with the abstract is:
  - Figure No.            ☐ as suggested by the applicant.
  - ☐ because the applicant failed to suggest a figure.
  - ☐ because this figure better characterizes the invention.
  - ☒ None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 94/01301

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 B01J20/18 B01D71/02 C01B33/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 B01J B01D C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 135 069 (SUZUKI HIROSHI) 27 March 1985 cited in the application see page 4, line 7 - page 27, line 6 ---	1,3
A	EP,A,0 481 660 (THE BRITISH PETROLEUM COMPANY P.L.C.) 22 April 1992 cited in the application see page 3, line 14 - page 5, line 11 ---	1,3
A	EP,A,0 397 216 (ALCAN INTERNATIONAL LIMITED) 14 November 1990 cited in the application see page 2, line 39 - page 3, line 23 ---	1,3
A	EP,A,0 149 343 (EXXON RESEARCH AND ENGINEERING COMPANY) 24 July 1985 see claim 1 ---	3
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \* "A" document defining the general state of the art which is not considered to be of particular relevance
- \* "E" earlier document but published on or after the international filing date
- \* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

\* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\* "A" document member of the same patent family

2

Date of the actual completion of the international search  17 August 1994	Date of mailing of the international search report  31.08.94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 cpo nl, Fax (+31-70) 340-3016	Authorized officer  Clement, J-P

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 94/01301

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 511 739 (NGK INSULATORS LTD) 4 November 1992 see page 4, line 22 - line 34 ----	3
A	US,A,5 019 263 (HAAG ET AL) 28 May 1991 see column 9, line 22 - column 10, line 39 ----	1,3
A	JOURNAL OF MEMBRANE SCIENCE, vol.73, 1992 pages 119 - 128 MENG-DONG JIA ET AL cited in the application see page 120, left column, line 32 - page 121, left column, line 5 -----	1,3

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 94/01301

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0135069	27-03-85	JP-A- 60028826 US-A- 4699892	14-02-85 13-10-87
EP-A-0481660	22-04-92	AU-A- 8473991 JP-A- 5043218	30-04-92 23-02-93
EP-A-0397216	14-11-90	AU-B- 597641 AU-A- 7155287 AU-B- 590700 AU-A- 7155487 EP-A, B 0242208 EP-A- 0242209 JP-A- 62279806 JP-A- 62294403 US-A- 4938870 US-A- 5137634	07-06-90 22-10-87 09-11-89 22-10-87 21-10-87 21-10-87 04-12-87 21-12-87 03-07-90 11-08-92
EP-A-0149343	24-07-85	CA-A- 1214448 JP-A- 60179136 US-A- 4578372	25-11-86 13-09-85 25-03-86
EP-A-0511739	04-11-92	JP-A- 5105420 US-A- 5266542	27-04-93 30-11-93
US-A-5019263	28-05-91	AU-B- 642499 AU-A- 7803791 CA-A- 2043592 EP-A- 0460512 JP-A- 4227826 US-A- 5100596 US-A- 5110478 US-A- 5069794	21-10-93 12-12-91 06-12-91 11-12-91 17-08-92 31-03-92 05-05-92 03-12-91

Form PCT/ISA/210 (patent family annex) (July 1992)

## PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

To:

BAWDEN, Peter, Charles  
Exxon Chemical Limited  
Exxon Chemical Technology Centre  
P.O. Box 1  
Abingdon  
Oxfordshire OX13 6BB  
ROYAUME-UNI

Date of mailing (day/month/year)	13 September 1994 (13.09.94)
Applicant's or agent's file reference	93A007
International application No.	PCT/EP94/01301
International filing date (day/month/year)	25 April 1994 (25.04.94)

## IMPORTANT NOTIFICATION

## 1. The following indications appeared on record concerning:

☒ the applicant    ☒ the inventor    ☐ the agent    ☐ the common representative

Name and Address

JACOBSON, Anne, Hershkowitz  
62 Hamilton Street  
Madison, NJ 07940  
United States of America

State of Nationality  
USState of Residence  
US

Telephone No.

Facsimile No.

Teleprinter No.

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person    ☐ the name    ☐ the address    ☐ the nationality    ☐ the residence

Name and Address

JACOBSON, Allan, Joseph  
3027 Lafayette Street  
Houston, TX 77005  
United States of America

State of Nationality  
GBState of Residence  
US

Telephone No.

Facsimile No.

Teleprinter No.

## 3. Further observations, if necessary:

## 4. A copy of this notification has been sent to:

<input checked="" type="checkbox"/> the receiving Office	<input checked="" type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input type="checkbox"/> the elected Offices concerned
<input type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

I. Hours

Telephone No. (41-22) 730.91.11

## PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

**PCT**NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

To:

BAWDEN, Peter, Charles  
Exxon Chemical Limited  
Exxon Chemical Technology Centre  
P.O. Box 1  
Abingdon  
Oxfordshire OX13 6BB  
ROYAUME-UNI

Date of mailing (day/month/year)	13 September 1994 (13.09.94)
Applicant's or agent's file reference 93A007	IMPORTANT NOTIFICATION
International application No. PCT/EP94/01301	International filing date 25 April 1994 (day/month/year) (25.04.94)

## 1. The following indications appeared on record concerning:

☒ the applicant ☒ the inventor ☐ the agent ☐ the common representative

Name and Address  LAI, Wenyth, Frank	State of Nationality	State of Residence
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☒ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address  LAI, Frank, Wenyih	State of Nationality	State of Residence
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 3. Further observations, if necessary:

## 4. A copy of this notification has been sent to:

☒ the receiving Office ☒ the designated Offices concerned  
☐ the International Searching Authority ☐ the elected Offices concerned  
☐ the International Preliminary Examining Authority ☐ other:

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

I. Hours

Telephone No. (41-22) 730.91.11

## PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION CONCERNING  
DOCUMENT TRANSMITTED

To:

United States Patent and Trademark  
Office  
(Box PCT)  
Washington D.C. 20231  
United States of America

in its capacity as elected Office

Date of mailing (day/month/year)

09 August 1995 (09.08.95)

International application No.

PCT/EP94/01301

International filing date (day/month/year)

25 April 1994 (25.04.94)

Applicant

EXXON CHEMICAL PATENTS INC. et al

The International Bureau transmits herewith the following documents and number thereof:

\_\_\_\_\_ copy of the international preliminary examination report (Article 36(3)(a))

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

S. Mafia

Telephone No.: (41-22) 730.91.11

## PCT COOPERATION TREA

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

United States Patent and Trademark  
Office  
Washington, D.C.

in its capacity as elected Office

Date of mailing:

24 November 1994 (24.11.94)

International application No.:

PCT/EP94/01301

Applicant's or agent's file reference:

93A007

International filing date:

25 April 1994 (25.04.94)

Priority date:

23 April 1993 (23.04.93)

Applicant:

DECKMAN, Harry, William et al

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

25 October 1994 (25.10.94)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

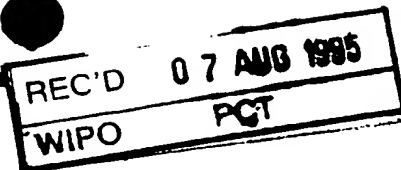
Authorized officer:

C. Combaz

Telephone No.: (41-22) 730.91.11

## PATENT COOPERATION TREATY

## PCT



## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>93A007</b>	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. <b>PCT/EP 94/ 01301</b>	International filing date (day/month/year) <b>25/04/1994</b>	Priority date (day/month/year) <b>23/04/1993</b>
International Patent Classification (IPC) or national classification and IPC <b>B01J20/18</b>		
Applicant <b>EXXON CHEMICAL PATENTS INC. et al.</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 10 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consists of a total of \_\_\_\_\_ sheets.

3. This report contains indications and corresponding pages relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☒ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand <b>25/10/1994</b>	Date of completion of this report <b>07. 08. 95</b>
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer  Telephone No. <b>R. Höfer</b>

**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**

Intern. application No.

PCT/EP94/01301

**I. Basis of the report**

1. This report has been drawn up on the basis of (Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.):

☒ the international application as originally filed.

☐ the description, pages \_\_\_\_\_, as originally filed,  
pages \_\_\_\_\_, filed with the demand,  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

☐ the claims, Nos. \_\_\_\_\_, as originally filed,  
Nos. \_\_\_\_\_, as amended under Article 19,  
Nos. \_\_\_\_\_, filed with the demand,  
Nos. \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
Nos. \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

☐ the drawings, sheets/fig \_\_\_\_\_, as originally filed,  
sheets/fig \_\_\_\_\_, filed with the demand,  
sheets/fig \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
sheets/fig \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

2. The amendments have resulted in the cancellation of:

☐ the description, pages \_\_\_\_\_.  
☐ the claims, Nos. \_\_\_\_\_.  
☐ the drawings, sheets/fig \_\_\_\_\_.

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Intern. application No.

PCT/EP94/01301

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been and will not be examined in respect of:

☐ the entire international application,

☒ claims Nos. 2-21 \_\_\_\_\_

because:

☐ the said international application, or the said claims Nos. \_\_\_\_\_ relate to the following subject matter which does not require an international preliminary examination (specify):

☒ the description, claims or drawings (indicate particular elements below) or said claims Nos. 1-21 \_\_\_\_\_ are so unclear that no meaningful opinion could be formed (specify):

The various definitions of the invention given in independent Claims 1,2,3,5,8-10 are such that the claims as a whole are not clear and concise, contrary to Article 6 PCT.

In the present case it is considered appropriate to use only one independent claim in any category.

Reference is made to the explanations given under chapter VIII.

☐ the claims, or said claims Nos. \_\_\_\_\_ are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for said claims Nos. \_\_\_\_\_.

**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**

Intern. application No.

PCT/EP94/01301

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**IV. Lack of unity of invention**

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1. In response to the invitation to restrict or pay additional fees the applicant has:

- ☐ restricted the claims.
- ☐ paid additional fees.
- ☐ paid additional fees under protest.
- ☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

- ☐ complied with.
- ☒ not complied with for the following reasons:

1.) The set of claims comprises seven independent claims which apparently define different groups of inventions.

The separate groups of inventions relate to the following different aspects:

- I) A supported zeolite layer comprising contiguous zeolite particles (claims 1 and 8)
- II) A supported zeolite layer not limited to a contiguous arrangement of the zeolite crystals, e.g. embedded in a matrix or (claims 2, 3, 5, 9 and 10).
- III: A process for preparation of a zeolite layer by crystallisation from a synthesis solution (claims 3, 9 and 10) and
- IV): A process for preparation of a zeolite layer by deposition of suspended crystallites (claim 5).

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Intern. application No.

PCT/EP94/01301

The common concept linking together the independent claims of group I) to IV) is the following:  
" An inorganic layer comprising crystalline molecular sieve on a support".

This common concept is known from D1 to D4, see e.g. document D1: claims 1 and 4; D2: claim 1; D3: example 1, comparative example B and figures 5, 29, D4: claim 1).

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

☐ all parts.

☒ the parts relating to claims Nos. 1\_\_\_\_\_.

**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**

Intern. application No.

PCT/EP94/01301

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement

**1. STATEMENT**

Novelty (N)	Claims _____	YES
	Claims 1 _____	NO
Inventive Step (IS)	Claims _____	YES
	Claims _____	NO
Industrial Applicability (IA)	Claims _____	YES
	Claims _____	NO

**2. CITATIONS AND EXPLANATIONS**

1.) The following documents have been considered for the purposes of this report:

D1: EP-A 511 739

D2: EP-A 135 069

D3: EP-A 481 660

D4: EP-A 149 343

1.) The present application does not satisfy the criterion set forth in Article 33(2) PCT because the subject-matter of claim 1 is not new in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT).

2.) D1 describes a layer of zeolite supported on a porous alumina substrate. The pores of the substrate have a diameter of 100 to 3000 nm (examples 1000 to 2000 nm). and the film of zeolite body is said to be formed in the pores and on the surface of the substrate with high density (D1: claims 1 and 4; page 2 line 50 to page 3,

line 12; page 5, table 1).

Therefrom it may be concluded that the mean particle size of the zeolite crystallites is below 1000nm and that the zeolite particles are arranged contiguous. Consequently the subject-matter of claim 1 is not new.

- 3.) In view of the objections raised under chapter IV and VIII it is not at present practicable to carry out a full examination of the application.

However, the applicant is informed that documents D1 to D4 could anticipate the patentability of any of the independent claims 2,3,5,9 and 10.

D2 discloses the preparation of an ultrathin layer of crystalline zeolite supported on a porous substrate by "in situ" synthesis/deposition of the zeolite on the substrate. The ultrathin layer has a thickness between one and several tens of nanometers, so that the zeolite crystallites are certainly smaller than 100 nm) ( D2: claim 1 ; page 4, lines 15-19; examples 1,4,7).

D3 discloses the preparation of a supported zeolite layer comprising crystallite of a size larger than 1000 nm. The zeolite layer is formed by crystallisation from a synthesis gel.

D4 describes the preparation of a supported zeolite layer by crystallisation from a synthesis solution.

The known products are suitable as selective membranes for separation of fluids and it appears that the thickness of the formed zeolite layer can also be controlled in the known processes.

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VII. Certain defects in the international application

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The following defects in the form or contents of the international application have been noted:

The references to the prior art document  
(PCT/EP92/02386) should be complemented with the number  
of the published document (WO-A ...).

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VIII. Certain observations on the international application

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The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

The various definitions of the invention given in independent claims 1-3, 5, 8-10 are such that the claims as a whole are not clear and concise, contrary to Article 6 PCT.

Claim 1 is limited to a supported inorganic layer comprising contiguous particles of a crystalline sieve.

Independent claims 2,3,5,8,9 and 10 are not limited to a such layer a contiguous arrangement of zeolite particles; claims 5 and 9 apparently relate to a layer comprising zeolite embedded in a matrix.

Independent claims 1,2,5 and 8 relate to supported zeolite layers comprising zeolite with specific, however different particle size ranges (20-1000 nm, 20-200 nm, smaller than 100 nm or of colloidal size).

Independent claims 3, 9 and 10 are not limited to a specific size of the zeolite particles.

The supported zeolite layer may be formed on the support by hydrothermal crystallisation from solution (claims 3 and 10) or by depositing suspended zeolite crystallites onto the support (claims 5 and 8) or by depositing and crystallizing zeolite crystallites onto the support (claim 9).

It is indicated in the description that the object of the application is to provide a supported molecular sieve layer of controllable thickness as well as process for preparation of such layers.

It is at present completely unclear which technical features are the essential to achieve this object.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>B01J 20/18, B01D 71/02, C01B 33/20</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/25151</b> <b>(43) International Publication Date:</b> 10 November 1994 (10.11.94)
<b>(21) International Application Number:</b> PCT/EP94/01301 <b>(22) International Filing Date:</b> 25 April 1994 (25.04.94) <b>(30) Priority Data:</b> 93303187.4 23 April 1993 (23.04.93) EP <b>(34) Countries for which the regional or international application was filed:</b> GB et al. <b>(71) Applicant (for all designated States except US):</b> EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> <u>DECKMAN, Harry</u> , William [US/US]; 4 Woods Edge Court, Clinton, NJ 08801 (US); <u>JACOBSON, Allan, Joseph</u> [GB/US]; 3027 Lafayette Street, Houston, TX 77005 (US); <u>McHENRY, James, Alexander</u> [US/US]; 4 Partridge Run, Washington, NJ 08801 (US); <u>KEIZER, Klaas</u> [NL/NL]; Benninkburg 19, NL-7511 MB Enschede (NL); <u>BURGGRAAF, Anthonie, Jan</u> [NL/NL]; Bastinglaan 15, NL-7548 AM Boekelo (NL); <u>VRON, Zeger, Alexander, Eduard, Pieter</u> [NL/NL]; Klimopstraat 14, NL-7552 SN Hengelo (NL); <u>CZARNETZKI, Lothar, Ruediger</u> [DE/NL]; Spanjaardslaan 19, NL-2352 AK Leiderdorp (NL); <u>LAL, Frank, Wenyh</u>		<b>[US/US];</b> 0-66 27th Street, Fair Lawn, NJ 07410 (US). <b>BONS, Antonie, Jan</b> [NL/BE]; Tiensesteenweg 259, B-3010 Kessel-Lo (BE); <b>MORTIER, Wilfried, Jozef</b> [NL/BE]; Diestse Steenweg 483, B-3010 Kessel-Lo (BE); <b>VERDUIN, Johannes, Petrus</b> [NL/BE]; Vlieguit 28, B-3061 Leefdaal (BE); <b>CORCORAN, Edward, William, Jr.</b> [US/US]; 2149 Stocker Mill Road, Easton, PA 18042 (US). <b>(74) Agents:</b> BAWDEN, Peter, Charles et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB). <b>(81) Designated States:</b> AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> MOLECULAR SIEVE LAYERS AND PROCESSES FOR THEIR MANUFACTURE <b>(57) Abstract</b> Layers comprising a molecular sieve layer on a porous or non-porous support, having uniform properties and allowing high flux are prepared from colloidal solutions of zeolite or other molecular sieve precursors (particle size less than 100 nm), by deposition, e.g., by spin or dipcoating, or by <i>in situ</i> crystallization.		

"Molecular Sieve Layers and Processes  
for their Manufacture"

This invention relates to molecular sieves, more especially to crystalline molecular sieves, and to layers containing them. More especially, the invention relates to a layer, especially a supported layer, containing particles of a crystalline molecular sieve.

Molecular sieves find many uses in physical, physicochemical, and chemical processes, most notably as selective sorbents, effecting separation of components in mixtures, and as catalysts. In these applications, the crystallographically-defined pore structure within the molecular sieve material is normally required to be open, and it is then a prerequisite that any structure-directing agent, or template, that has been employed in the manufacture of the molecular sieve be removed, usually by calcination.

Numerous materials are known to act as molecular sieves, among which zeolites form a well-known class. Examples of zeolites and other materials suitable for use in the invention will be given below.

When molecular sieves are used as sorbents or catalysts they are often in granular form. Such granules may be composed entirely of the molecular sieve or be a composite of a binder or support and the molecular sieve, with the latter distributed throughout the entire volume of the granule. In any event, the granule usually contains a non-molecular sieve pore structure which improves mass transfer through the granule.

The support may be continuous, e.g., in the form of a plate, or it may be discontinuous, e.g., in the form of granules. The molecular sieve crystals may be of such a size that, although the pores of the support are occupied by the crystals, the pores remain open. Alternatively, the molecular sieve may occupy the pores to an extent that the pores are effectively closed; in this case, when the

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support is continuous a molecular sieve membrane may result.

Thus, depending on the arrangement chosen and the nature and size of the material to be contacted by the molecular sieve, material may pass through the bulk of the molecular sieve material entirely through the pores of the molecular sieve material, or entirely through interstices between individual particles of the molecular sieve material, or partly through the pores and partly through the interstices.

Molecular sieve layers having the permeation path entirely through the the molecular sieve crystals have been proposed for a variety of size and shape selective separations. Membranes containing molecular sieve crystals have also been proposed as catalysts having the advantage that they may perform catalysis and separation simultaneously if desired.

In EP-A-135069, there is disclosed a composite membrane comprising a porous support, which may be a metal, e.g., sintered stainless steel, an inorganic material, or a polymer, one surface of which is combined with an ultra thin (less than 25 nm) film of a zeolite. In the corresponding U.S. Patent No. 4,699,892, it is specifically stated that the zeolite is non-granular. In EP-A-180200, a composite membrane is disclosed, employing a zeolite that has been subjected to microfiltration to remove all particles of 7.5 nm and above. The membrane is made by impregnation of a porous support by the ultrafiltered zeolite solution, resulting in a distribution of the zeolite crystals within the pore structure.

In EP-A-481660, which contains an extensive discussion of earlier references to membranes, there is disclosed a zeolite membrane on a porous support, in which the zeolite crystals are stated to form an essentially continuous layer over and be directly bonded to the support. The membrane is formed by immersing the support in a synthesis gel, multiple immersions being employed to ensure that any

pinholes are occluded by the zeolite crystals being formed within the pores.

Zeolites with a small particle size and narrow size distribution are disclosed for use in composite poly-dimethylsiloxane membranes in J. Mem. Sci. 73 (1992) p119 to 128, by Meng-Dong Jia et al; however, the crystal size, though uniform, is within the range of 200 to 500 nm. Bein et al, in Zeolites, Facts, Figures, Future, Elsevier, 1989, pp 887 to 896, disclose the manufacture of zeolite Y crystals of a size of about 250 nm and embedding them in a glassy silica matrix. Even smaller sizes such as 2 to 10 nm are envisaged in WO 92/19574.

In Zeolites, 1992, Vol. 12, p 126, Tsikoyiannis and Haag describe the formation of membranes from zeolite synthesis gels on both porous and non-porous supports; when the support is non-porous, e.g., poly-tetrafluorethylene or silver, the membrane is separable from the support. When the support is porous, e.g., a Vycor (a trademark) porous glass disk, the membrane is strongly bonded to the surface, zeolite crystallization within the pores being prevented by presoaking the disk in water.

Numerous other techniques for forming membranes have been proposed.

In EP-A-397216, methods of making crack- and pinhole-free alumina films of a thickness within the range of from 0.01 to 2  $\mu$ m on a porous support layer are described, the methods including brush, spray, dip, spincoating, electrophoretic and thermophoretic techniques. The membranes may be pretreated.

Despite the proposals in these literature and patent references, there still remains a need for a supported inorganic molecular sieve layer having a controllable thickness that may, if desired, be of a thickness of the order of only a few microns. There accordingly also remains a need for a process of manufacturing such a layer whereby the uniformity of the layer thickness may be controlled, even when the layer is thin.

Such a layer and a process for its manufacture make possible the production of a number of useful products, including membranes, which because of their uniformity and thinness will have predictable properties, and will permit a high flux.

It has now been found that such a supported layer is obtainable using as starting material a crystalline molecular sieve of very small particle size, preferably of a size that a true colloidal dispersion of the particles may be obtained, and preferably also of a narrow particle size distribution.

In a first aspect of the invention, there is provided a layer comprising a supported inorganic layer comprising contiguous particles of a crystalline molecular sieve, the particles having a mean particle size within the range of from 20 nm to 1  $\mu$ m.

Advantageously, in the first aspect of the invention, the mean particle size is within the range of from 20 to 500 nm, preferably it is within the range of from 20 to 300 nm and most preferably within the range of from 20 to 200 nm. Alternatively, the mean particle size is advantageously such that at least 5% of the unit cells of the crystal are at the crystal surface.

In a second aspect of the invention, there is provided a supported inorganic layer comprising particles of a crystalline molecular sieve, the particles having a mean particle size within the range of from 20 to 200 nm.

In both the first and second aspects of the invention, the layer comprises molecular sieve particles optionally coated with skin of a different material; these are identifiable as individual particles (although they may be intergrown as indicated below) by electron microscopy. The layer, at least after activation, is mechanically cohesive and rigid. Within the interstices between the particles in this rigid layer, there may exist a plethora of non-molecular sieve pores, which maybe open, or partially open, to permit passage of material through or within the layer,

or may be completely sealed, permitting passage through the layer only through the pores in the particles.

Advantageously, the particle size distribution is such that 95% of the particles have a size within  $\pm 33\%$  of the mean, preferably 95% are within  $\pm 15\%$  of the mean, preferably  $\pm 10\%$  of the mean and most preferably 95% are within  $\pm 7.5\%$  of the mean.

It will be understood that the particle size of the molecular sieve material forming the layer may vary continuously or stepwise with distance from the support. In such a case, the requirement for uniformity is met if the particle size distribution is within the defined limit at one given distance from the support, although advantageously the particle size distribution will be within the defined limit at each given distance from the support.

The use of molecular sieve crystals of small particle size and preferably of homogeneous size distribution facilitates the manufacture of a three-dimensional structure which may if desired be thin but which is still of controlled thickness.

In the first aspect of the invention, the particles are contiguous, i.e., substantially every particle including any skin that may be present is in contact with one or more of its neighbours as evidenced by electron microscopy preferably high resolution microscopy, although not necessarily in contact with all its closest neighbours. Such contact may be such in some embodiments that neighbouring crystal particles are intergrown, provided they retain their identity as individual crystalline particles. Advantageously, the resulting three dimensional structure is grain-supported, rather than matrix-supported, in the embodiments where the layer does not consist essentially of the crystalline molecular sieve particles. In a preferred embodiment, the particles in the layer are closely packed.

In the second aspect of the invention, the particles may be contiguous, but need not be.

A layer in accordance with either the first or the second aspect of the invention may be constructed to contain passageways, between the particles, that provide a non-molecular sieve pore structure through or into the layer. Such a layer may consist essentially of the particles or may contain another component, which may be loosely termed a matrix which, while surrounding the particles, does not so completely or closely do so that all pathways round the particles are closed. Alternatively, the layer may be constructed so that a matrix present completely closes such pathways, with the result that the only path through or into the layer is through the particles themselves.

It will be understood that references herein to the support of a layer include both continuous and discontinuous supports.

References to particle size are throughout this specification to the longest dimension of the particle and particle sizes are as measured by direct imaging with electron microscopy. Particle size distribution may be determined by inspection of scanning or transmission electron micrograph images preferably on lattice images, and analysing an appropriately sized population of particles for particle size.

As molecular sieve, there may be mentioned a silicate, metallosilicates, an aluminosilicate, an aluminophosphate, a silicoaluminophosphate, a metalloaluminophosphate, a metalloaluminophosphosilicate or a gallosilicate.

The preferred molecular sieve will depend on the chosen application, for example, separation, catalytic applications, and combined reaction separation. There are many known ways to tailor the properties of the molecular sieves, for example, structure type, chemical composition, ion-exchange, and activation procedures.

Representative examples are molecular sieves/zeolites of the structure types AFI, AEL, BEA, CHA, EUO, FAU, FER, KFI, LTA, LTL, MAZ, MOR, MFI, MEL, MTW, OFF and TON.

Some of the above materials while not being true zeolites are frequently referred to in the literature as such, and this term will be used broadly in the specification below.

A supported layer according to the invention may be manufactured in a number of different ways. In one embodiment the invention provides a process of making a layer by deposition on a support from a colloidal zeolite suspension obtainable by preparing an aqueous synthesis mixture comprising a source of silica and an organic structure directing agent in a proportion sufficient to effect substantially complete dissolution of the silica source in the mixture at the boiling temperature of the mixture, and crystallization from the synthesis mixture. The synthesis mixture will contain, in addition, a source of the other component or components, if any, in the zeolite.

The particle size of the crystals formed may be controlled by the crystallization temperature, or any other process capable of giving crystals of highly uniform particle size, in a size such that a stable colloidal suspension may be obtained. A stable colloidal suspension is one in which no visible separation occurs on standing for a prolonged period, e.g., one month. Details of a procedure for preparing the colloidal suspension mentioned above are given in our co-pending Application No. PCT/EP92/02386, the entire disclosure of which is incorporated by reference herein.

The invention also provides a supported layer made by the above process.

In accordance with preferred processes according to the invention, the silica is advantageously introduced into the synthesis mixture as silicic acid powder.

The organic structure directing agent is advantageously introduced into the synthesis mixture in the form of a base, specifically in the form of a hydroxide, but a salt, e.g., a halide, especially a bromide, may be employed.

The structure directing agent may be, for example, the hydroxide or salt of tetramethylammonium (TMA), tetraethylammonium (TEA), triethylmethylammonium (TEMA), tetrapropylammonium (TPA), tetrabutylammonium (TBA), tetrabutylphosphonium (TBP), trimethylbenzylammonium (TMBA), trimethylcetylammmonium (TMCA), trimethylneopentylammonium (TMNA), triphenylbenzylphosphonium (TPBP), bispyrrolidinium (BP), ethylpyridinium (EP), diethylpiperidinium (DEPP) or a substituted azoniabicyclooctane, e.g. methyl or ethyl substituted quinuclidine or 1,4-diazoniabicyclo-(2,2,2) octane.

Preferred structure directing agents are the hydroxides of TMA, TEA, TPA and TBA.

Further processes for the manufacture of layers according to the invention, including specific methods of depositing the molecular sieve on the support and post-treatment of the resulting layer, will be given below.

The thickness of the molecular sieve layer is advantageously within the range of 0.1 to 20  $\mu\text{m}$ , preferably 0.1 to 15  $\mu\text{m}$ , more preferably from 0.1 to 2  $\mu\text{m}$ . Advantageously, the thickness of the layer and the particle size of the molecular sieve are such that the layer thickness is at least twice the particle size, resulting in a layer several particles thick rather than a monolayer of particles.

Advantageously, the layer is substantially free of pinholes, i.e., substantially free from apertures of greatest dimension greater than 0.1  $\mu\text{m}$ . Advantageously, at most 0.1% and preferably at most 0.0001% of the surface area is occupied by such apertures.

Depending on the intended end use of the layer, a greater or smaller proportion of the area of the layer may

be occupied by macropores, apertures having a greatest dimension less than  $0.1\text{ }\mu\text{m}$  but greater than  $1\text{ nm}$ . These macropores may be formed by the interstices between the crystals of the molecular sieve, if the layer consists essentially of the molecular sieve, and elsewhere, if the layer comprises the molecular sieve and other components. Such layers may be used, inter alia, for ultrafiltration, catalytic conversion, and separations based on differences in molecular mass (Knudsen diffusion), and indeed for any processes in which a high surface area is important.

The layer advantageously has a large proportion of its area occupied by crystalline-bounded micropores, i.e., pores of a size between  $0.2$  and  $1\text{ nm}$ , depending on the particular molecular sieve being employed. Pores of size within the micropore range result, for example, when the layer contains a component in addition to one derived from colloidal molecular sieve particles. In another embodiment especially suitable for ultrafiltration, the layer contains nanopores, i.e., pores of a size between  $1$  and  $10\text{ nm}$ .

The layer support may be either non-porous or, preferably, porous, and may be continuous or particulate. As examples of non-porous supports there may be mentioned glass, fused quartz, and silica, silicon, dense ceramic, for example, clay, and metals. As examples of porous supports, there may be mentioned porous glass, sintered porous metals, e.g., steel or nickel (which have pore sizes typically within the range of  $0.2$  to  $15\text{ }\mu\text{m}$ ), and, especially, an inorganic oxide, e.g., alpha-alumina, titania, an alumina/zirconia mixture, or Cordierite.

At the surface in contact with the layer, the support may have pores of dimensions up to 50 times the layer thickness, but preferably the pore dimensions are comparable to the layer thickness.

Advantageously, the support is porous alpha-alumina. Typically this has a surface pore size within the range of from  $0.08$  to  $10\text{ }\mu\text{m}$ , preferably from  $0.08$  to  $1\text{ }\mu\text{m}$ , most

preferably from 0.08 to 0.16  $\mu\text{m}$ , and advantageously with a narrow pore size distribution. The support may be multilayered; for example, to improve the mass transfer characteristics of the layer, only the surface region of the support in contact with the layer may have small diameter pores, while the bulk of the support, toward the surface remote from the layer, may have large diameter pores. An example of such a multilayer support is an alpha-alumina disk having pores of about 1  $\mu\text{m}$  diameter coated with a layer of alpha-alumina with pore size about 0.08  $\mu\text{m}$ .

The invention also provides a structure in which the support, especially a continuous porous support, has a molecular sieve layer on each side of the support, the layers on the two sides being the same or different.

The layer may, and for many uses advantageously does, consist essentially of the molecular sieve material, or it may be a composite of the molecular sieve material and intercalating material which is also inorganic. The intercalating material may be the material of the support. If the layer is a composite it may, as indicated above, contain macropores and/micropores, bounded by molecular sieve portions, by portions of intercalating material, or by both molecular sieve and intercalating material. The material may be applied to the support simultaneously with or after deposition of the molecular sieve, and may be applied, for example, by a sol-gel process followed by thermal curing. Suitable materials include, for example, inorganic oxides, e.g., silica, alumina, and titania.

The intercalating material is advantageously present in sufficiently low a proportion of the total material of the layer that the molecular sieve particles remain contiguous.

The invention further provides additional preferred processes for manufacturing a layer.

The present invention accordingly also provides a process for the manufacture of a layer comprising a

crystalline molecular sieve on a porous support, which comprises pre-treating the porous support to form at a surface thereof a barrier layer, and applying to the support a reaction mixture comprising a colloidal suspension of molecular sieve crystals, having a mean particle size of at most 100 nm and advantageously a particle size distribution such that at least 95% of the particles have a size within  $\pm 15\%$ , preferably  $\pm 10\%$ , more preferably within  $\pm 7.5\%$ , of the mean, colloidal silica and optionally an organic structure directing agent, to form a supported molecular sieve layer, and if desired or required activating the resulting layer.

Activation removes the template and can be achieved by calcination, ozone treatment, plasma treatment or chemical extraction such as acid extraction.

The invention also provides a supported layer formed by the process.

The barrier layer functions to prevent the water in the aqueous reaction mixture from preferentially entering the pores of the support to an extent such that the silica and zeolite particles form a thick gel layer on the support.

The barrier layer may be temporary or permanent. As a temporary layer, there may be mentioned an impregnating fluid that is capable of being retained in the pores during application of the reaction mixture, and readily removed after such application and any subsequent treatment.

As indicated below, spin coating is an advantageous technique for applying the reaction mixture to the support according to this and other aspects of the invention. The impregnating fluid should accordingly be one that will be retained in the pores during spinning if that technique is used; accordingly the rate of rotation, pore size, and physical properties of the fluid need to be taken into account in choosing the fluid.

The fluid should also be compatible with the reaction mixture, for example if the reaction mixture is polar, the

barrier fluid should also be polar. As the reaction mixture is advantageously an aqueous reaction mixture, water is advantageously used as the barrier layer.

To improve penetration, the fluid barrier may be applied at reduced pressure or elevated temperature. If spin-coating is used, the support treated with the barrier fluid is advantageously spun for a time and at a rate that will remove excess surface fluid, but not remove fluid from the pores. Premature evaporation of fluid from the outermost pores during treatment may be prevented by providing an atmosphere saturated with the liquid vapour.

As a temporary barrier layer suitable, for example, for an alpha-alumina support there may be especially mentioned water or glycol. As a permanent barrier suitable for an alpha-alumina support there may be mentioned titania, gamma-alumina or an alpha-aluminacoating of smaller pore size.

The colloidal suspension of molecular sieve crystals is advantageously prepared by the process indicated above, i.e., that described in PCT Application EP/92/02386. The colloidal silica may be prepared by methods known in the art; see for example Brinker and Scherer, Sol-Gel Science, Academic Press, 1990. A preferred method is by the acid hydrolysis of tetraethyl Orthosilicate. The organic structure directing agent, if used, is advantageously one of those mentioned above.

As indicated above, the reaction mixture is advantageously applied to the support by spin-coating, the viscosity of the mixture and the spin rate controlling coating thickness. The mixture is advantageously first contacted with the stationary support, then after a short contact time the support is spun at the desired rate. After spinning, the silica is advantageously aged by retaining the supported layer in a high humidity environment, and subsequently dried, advantageously first at room temperature and then in an oven.

In a further embodiment of the invention, there is provided a process for the manufacture of a layer comprising a crystalline molecular sieve on a porous support which comprises applying to the support by dip-coating a colloidal suspension of molecular sieve crystals, having a mean particle size of at most 100 nm and advantageously a particle size distribution such that at least 95% of the particles have a size within  $\pm 15\%$ , preferably  $\pm 10\%$ , more preferably  $\pm 7.5\%$ , of the mean, drying the resulting gel on the support and if desired or required activating the resulting layer.

The invention also provides a layer made by the process.

In this embodiment of the invention, the pH of the suspension is an important factor. For example, at a pH above 12, colloidal silicalite crystals tend to dissolve in the medium. Adhesion of the layer to the support improves as pH is reduced, with acceptable adhesion being obtained between pH 7 and 11, good adhesion between pH 4.0 and 7, and very good adhesion below pH 4.0, although agglomeration of particles may occur at too low a pH.

Adhesion of the layer to its support may be enhanced by the inclusion in the suspension of an organic binder or surfactant, the presence of an appropriate proportion of which may also reduce the incidence of cracks in the final layer. Among binders there may be mentioned polyvinyl alcohol (PVA), advantageously with a molecular weight of from 1000 to 100000, preferably from 2000 to 10000, and most preferably in the region of 3000, and hydroxyalkyl cellulose, especially hydroxypropyl cellulose (HPC), advantageously with a molecular weight of from 50000 to 150000, and preferably in the region of 100000.

An appropriate proportion of crystals in the suspension may readily be determined by routine experiment; if the proportion is too low a continuous layer will not be reliably formed while if it is too high the layer will tend to contain cracks after activation. For silicalite,

advantageous lower and upper limits are 0.5% (preferably 0.75%) and 1.5% respectively.

The time spent by the support immersed in the suspension also affects the thickness of the layer and its quality. Advantageously the dip-time is at most 15 seconds with a solution containing 1.1% by weight silicalite crystals; an immersion of from 1 to 10 seconds gives a crack-free layer of thickness 0.7 to 3  $\mu\text{m}$ .

In our co-pending Application No. PCT/EP92/02330, the entire disclosure of which is incorporated by reference herein, there is disclosed the formation of an aqueous synthesis mixture comprising a source of particulate silica in which the particles advantageously have a mean diameter of at most 1  $\mu\text{m}$ , seeds of an MFI zeolite having a mean particle size of at most 100 nm in the form of a colloidal suspension, an organic structure directing agent, and a source of fluorine or of an alkali metal, the synthesis mixture having an alkalinity, expressed as a molar ratio of  $\text{OH}^-:\text{SiO}_2$  of at most 0.1. Crystallization of this synthesis mixture produces very uniform, small, zeolite crystals. The proportion of seed, based on the weight of the mixture, is given as from 0.05 to 1700 wppm. The synthesis mixture will additionally contain a source of any other zeolite component.

In a further embodiment of the present invention, a seeding technique may be used. In this embodiment, the invention provides a process for the manufacture of a layer comprising a crystalline molecular sieve on a porous support, which comprises applying to or forming on the support a layer comprising amorphous silica containing seeds of a zeolite having a mean particle size of at most 100 nm, and advantageously having a particle size distribution such that at least 95% of the particle have a size within  $\pm 15\%$ , preferably  $\pm 10\%$ , preferably within  $\pm 7.5\%$ , of the mean, subjecting the layer to hydrothermal crystallization, and if desired or required activating the crystallized layer.

Again, other components useful in forming the zeolite layer may be present. Such components may include, for example, an organic structure directing agent, which may be in salt form.

The invention also provides a supported layer made by the process.

The layer is advantageously applied to or formed on the support by dipcoating or spincoating, advantageously substantially as described above.

If dipcoating is used, the support is advantageously dipped into a solution containing the amorphous silica in colloidal form, advantageously with a particle size at most 0.1  $\mu\text{m}$ ; the solution may if desired contain other components useful in forming the final zeolite layer. If spincoating is used, the silica may be of larger particle size but is advantageously colloidal.

The layer thickness at this stage, after dipcoating or spincoating, is advantageously within the range of from 0.1 to 20  $\mu\text{m}$ .

Hydrothermal crystallization to form the zeolite layer is advantageously carried out by immersing the layer in a solution described below, and heating for time and at the temperature necessary to effect crystallization.

The solution advantageously contains either all the components necessary to form a zeolite or only those components necessary but which are not already present in the layer on the support. In the latter case, crystals do not form in the solution, which remains clear and maybe re-used.

After crystallization, the supported layer may be washed, dried, and activated in the normal way.

By this embodiment of the invention, a dense, homogeneous, and crack-free supported layer may be obtained. A 1  $\mu\text{m}$  thick zeolite layer may readily be obtained, with a grain size of 100 to 300 nm.

In a further embodiment of the invention, molecular sieve crystals are synthesized in situ on the support.

According to this embodiment, the invention provides a process for the manufacture of a layer comprising a crystalline molecular sieve on a porous support, which comprises preparing a synthesis mixture comprising a source of silica and an organic structure directing agent preferably in the form of a hydroxide in a proportion sufficient to effect substantially complete dissolution of the silica source in the mixture at the boiling temperature of the mixture, immersing the support in the synthesis mixture, crystallizing zeolite from the synthesis mixture onto the support, and if desired or required activating the crystallized layer.

The invention also provides a supported layer made by the process.

The synthesis mixture will also contain a source of other components, if any, in the zeolite.

Advantageously, to obtain colloidal material, crystallization is effected at a temperature less than 120° C. As indicated in PCT/EP92/02386, the lower the crystallization temperature the smaller the resulting particle size of the crystals. For zeolites made in the presence of an alumina source, the particle size may also be varied by varying the alumina content. The effect of varying the alumina content is, however, not the same for all zeolites; for example, for zeolite beta, the particle size varies inversely with alumina content while for an MFI-structured zeolite the relationship is direct.

The substrate used in accordance with this aspect of the invention may be any one of those described above in connexion with other processes; an alpha-alumina support is advantageously used; the pore size may vary with the intended use of the layer; a pore size within the range 100 nm to 1.5  $\mu$ m may conveniently be used. Care should be taken to avoid undue weakening of the support by, for example, controlling prolonged exposure to high temperatures and alkalinity.

Although the various processes of the invention described above yield a supported layer of good quality, the resulting layer may still contain apertures of greater size than desired for the intended use of the product. For example, apertures greater than those through the molecular sieve itself are undesirable if the supported layer is to be used for certain types of separation process since they result in a flux greater than desired and impaired separation. If this is the case, the supported layer may be subjected to a reparation procedure. In this procedure, the supported layer may be subjected to one of the various reparation techniques known to those skilled in the art.

It is therefore in accordance with the invention to manufacture a supported layer by first carrying out one of the layer-forming processes according to the invention and described above and following it by reparation of the layer by a method known per se.

Preferably, however, the reparation is carried out by again subjecting the supported layer to a manufacturing process of the invention.

The invention accordingly also provides a process for the manufacture of a supported layer in which one of the layer-forming processes above is carried out two or more times, or in which one of the processes above carried out one or more times is followed by another of the processes above, carried out one or more times, or in which one of the processes above is carried out two or more times with another or others of the processes above, carried out one or more times, intervening. The invention also provides a supported layer, especially a membrane, made by such a process.

The layers according to the invention and produced in accordance with the processes of the invention may be treated in manners known per se to adjust their properties, e.g., by steaming or ion exchange to introduce different cations or anions, by chemical modification, e.g.,

deposition of organic compounds on the crystals or into the pores of the molecular sieve, or by introduction of a metal.

The layers may be used in the form of a membrane, used herein to describe a barrier having separation properties, for separation of fluid (gaseous, liquid, or mixed) mixtures, for example, separation of a feed for a reaction from a feedstock mixture, or in catalytic applications, which may if desired combine catalysed conversion of a reactant or reactants and separation of reaction products.

Separations which may be carried out using a membrane comprising a layer in accordance with the invention include, for example, separation of normal alkanes from co-boiling hydrocarbons, for example normal alkanes from iso alkanes such as in  $C_4$  to  $C_6$  mixtures and  $n-C_{10}$  to  $C_{16}$  alkanes from kerosene; separation of aromatic compounds from one another, especially separation of  $C_8$  aromatic isomers from each other, more especially para-xylene from a mixture of xylenes and, optionally, ethylbenzene, and separation of aromatics of different carbon numbers, for example, mixtures of benzene, toluene, and mixed  $C_8$  aromatics; separation of aromatic compounds from aliphatic compounds, especially aromatic molecules with from 6 to 8 carbon atoms from  $C_5$  to  $C_{10}$  (naphtha range) aliphatics; separation of olefinic compounds from saturated compounds, especially light alkenes from alkane/alkene mixtures, more especially ethene from ethane and propene from propane; removing hydrogen from hydrogen-containing streams, especially from light refinery and petrochemical gas streams, more especially from  $C_2$  and lighter components; and alcohols from aqueous streams.

Separation of heteroatomic compounds from hydrocarbons such as alcohols and sulphur containing materials such as  $H_2S$  and mercaptans.

The supported layer of the invention may be employed as a membrane in such separations without the problem of being damaged by contact with the materials to be separated. Furthermore, many of these separations are

carried out at elevated temperatures, as high as 500°C, and it is an advantage of the supported layer of the present invention that it may be used at such elevated temperatures.

The present invention accordingly also provides a process for the separation of a fluid mixture which comprises contacting the mixture with one face of a layer according to the invention in the form of a membrane under conditions such that at least one component of the mixture has a different steady state permeability through the layer from that of another component and recovering a component or mixture of components from the other face of the layer.

Some specific reaction systems where these membranes would be advantageous for selective separation either in the reactor or on reactor effluent include: selective removal of a Para-Xylene rich mixture from the reactor, reactor product, reactor feed or other locations in a Xylenes isomerization process; selective separation of aromatics fractions or specific aromatics molecule rich streams from catalytic reforming or other aromatics generation processes such as light alkane and alkene dehydrocyclization processes (e.g. C<sub>3</sub>-C<sub>7</sub> paraffins to aromatics from processes such as Cyclar), methanol to gasoline and catalytic cracking processes; selective separation of benzene rich fractions from refinery and chemical plant streams and processes; selective separation of olefins or specific olefin fractions from refinery and chemicals processing units including catalytic and thermal cracking, olefins isomerization processes, methanol to olefins processes, naphtha to olefins conversion processes, alkane dehydrogenation processes such as propane dehydrogenation to propylene; selective removal of hydrogen from refinery and chemicals streams and processes such as catalytic reforming, alkane dehydrogenation, catalytic cracking, thermal cracking, light alkane/alkene dehydrocyclization, ethylbenzene dehydrogenation, paraffin dehydrogenation; selective separation of molecular isomers

in processes such as butane isomerization, butylene isomerization, paraffin isomerization, olefin isomerization; selective separation of alcohols from aqueous streams and/or other hydrocarbons; selective separation of products of bimolecular reactions where equilibrium limits conversion to the desired products, e.g. MTBE production from methanol and isobutylene, ethylbenzene from ethylene and benzene, and cumene from propylene and benzene; selective removal of 2,6 dimethyl naphthalene from mixtures of alkane substituted naphthalenes during alkylation and/or isomerization.

The invention further provides a process for catalysing a chemical reaction which comprises contacting a feedstock with a layer according to the invention which is in active catalytic form under catalytic conversion conditions and recovering a composition comprising at least one conversion product.

The invention further provides a process for catalysing a chemical reaction which comprises contacting a feedstock with one face of a layer according to the invention, that is in the form of a membrane and in active catalytic form, under catalytic conversion conditions, and recovering from an opposite face of the layer at least one conversion product, advantageously in a concentration differing from its equilibrium concentration in the reaction mixture.

The following examples illustrate the invention:

#### Example 1

This example illustrates manufacture of a layer by spin-coating with a temporary barrier layer.

A porous alpha-alumina disk, diameter 25 mm, thickness 3 mm, pore size 80 nm, is soaked in demineralized water for 3 days. The soaked disk is placed in the specimen chuck of a CONVAC Model MTS-4 Spinner, and hot water is placed in the process cup to increase the humidity of the atmosphere. The disk is spun at 4000 rpm for 30 seconds.

The disk is then immediately covered with a slurry comprising 25% by weight of Ludox (a trademark) AS-40 colloidal silica and 75% by weight of an aqueous dispersion containing 6.5% by weight colloidal silicalite (MFI) zeolite, mean particle size 50 nm. 10 seconds after contact between the slurry and the disk, the disk is spun at 4000 rpm for 30 seconds. The disk and the resulting silica-zeolite layer are kept in a closed vessel at relative humidity close to 100% for 3 hours to age the silica, air dried at room temperature for 2 hours and subsequently in an oven at 110°C for 2 hours.

Under an optical microscope, the resulting silica-zeolite layer appeared smooth, crack-free, and homogeneous. Scanning Electron Microscopy (SEM) of across-section through the supported layer shows a layer about 1  $\mu\text{m}$  thick containing uniformly sized zeolite particles - see Fig. 1. The homogeneity and continuity of the layer, coupled with its thinness, confirm that the resulting structure after calcining will form a layer according to the invention.

In a comparison experiment, instead of soaking the disk, it was dried at 150°C in air for 12 hours, other process steps remaining the same. As can be seen from the SEM cross section shown in Fig. 2, the resulting layer is about 40  $\mu\text{m}$  thick. It is also cracked, and not firmly attached to the substrate, making it unsuitable for use as a layer.

#### Example 2

This example illustrates manufacture of a layer by spin-coating using a permanent barrier layer.

The support comprised an alpha-alumina base with a barrier layer of gamma-alumina, and was prepared as follows:

A slurry was prepared by ball milling 800 g  $\text{Al}_2\text{O}_3$  in 500 ml distilled water containing 4.3 ml hydrochloric acid for 16 hours to give alumina particles of mean diameter 0.5  $\mu\text{m}$ . The slurry was degassed, poured into moulds and allowed to dry at ambient temperature for 3 days. The cast

pieces were heated at 5°C/min to 1200°C, then fired at 1200°C for 2 hours. The fired pieces were then polished front and back to a thickness of about 3 mm. A gamma-alumina coating was applied by dipping the alpha-alumina piece once into a colloidal suspension of Boehmite, prepared by hydrolysis of alumina sec-butoxide in 600 ml water and 0.76 ml nitric acid. The Boehmite layer was converted to gamma-alumina by heating to 400°C at a rate of 10°C/hour and holding for 24 hours. The coated product provides a support.

A silica sol was prepared from tetraethylortho-silicate, water, and hydrochloric acid and aged at 50°C for 90 minutes.

A suspension of silicalite 1, mean particle size 55 nm, particle size range 40 to 70 nm, containing 8.7% by weight colloidal crystals in aqueous TPAOH, pH 10.3, was prepared and a coating slurry formed by mixing equal weights of the suspension and the sol. The resulting slurry was spin-coated onto the support at 4000 rpm.

The resulting structure was then heated to 600°C at a heating rate of 20°C/hour. The final layer structure is shown edge on and from the top surface in Figures 3 and 4. The edge on view demonstrates that the layer thickness is about 0.2  $\mu\text{m}$  and the top view shows the organization of the crystals in the layer, and that the crystals are incorporated into the layer with little or no change in crystal size and shape.

### Example 3

This example illustrates the use of a layer according to the invention in the separation of a hydrocarbon mixture.

The layer of Example 2 was used to separate an equimolar mixture of toluene, m-xylene, n-octane and iso-octane. The mixture was applied to the layer side of the layer structure in a continuous flow. A gas sweep (Argon 40-500 ml/min) was applied to the support side of the layer structure, and sampled by a gas operating with a 10' x 1/8" (about 3 m x 3 mm) stainless steel, GP5% SP1200/ 5% Bentone

34 on 100/120 Supelcoport column. The total pressure drop across the layer was 1000 kPa. Analysis of the gc data shows that the layer permeate had an enhanced aromatics content relative to feed content. Representative data at a temperature of 180°C are shown in Figure 5. The plot shows the relative concentrations of toluene, m-xylene, n-octane and iso-octane as a function of elapsed time. The largest separation factor is observed for toluene/iso-octane with a value of 10. The total flux of hydrocarbon through the layer corresponds to 100 kg/m<sup>2</sup>/day at the start and after 16 hours to an average of 40 kg/m<sup>2</sup>/day.

#### Examples 4 to 26

These examples illustrate manufacture of a layer by dip-coating.

In each of the following Examples, a colloidal MFI zeolite crystal suspension having a mean particle size of 70 nm was employed, together with a gamma-alumina surfaced alpha-alumina support as described in Example 2. After dipping, the supported layer was dried at 40°C for 3 hours, at a relative humidity of 60%. Each layer was heated at 10° C/hour to 550°C, maintained at that temperature for 3 hours to effect calcination, and cooled to room temperature at 20° C/hour.

#### Examples 4 to 9

These examples were conducted at a dip time of 5 seconds, a concentration of zeolite of 1.1%, and 1.6 g/l of hydroxypropyl cellulose, varying the pH by adding small amounts of a one molar HNO<sub>3</sub> solution, the effect of pH on adhesion being shown.

<u>Example No</u>	<u>pH</u>	<u>Adhesion</u>
4	3.6	very good
5	5.2	good
6	7.6	acceptable
7	9.1	acceptable
8	10.6	acceptable
9	11.7	poor

Observation of adhesion standard was subjective; the zeolite layer thickness varied between 1.5 and 2  $\mu\text{m}$ , as determined by S.E.M.

Examples 10 to 14

These examples were conducted at a dip time of 5 seconds, a zeolite concentration of 1.1%, a pH of 3.5, and with different binders/surfactants.

Example No.	Additive	Conc. g/l	Observation Ad;Conty
10	PVA, M = 72000	20	very bad; cracks
11	PVA, M = 3000	20	acceptable; cont.
12	HPC, M = 100000	1.6	very good; cont.
13	PVA, M = 3000	20 }	good; cont.
	HPC, M = 100000	1.6 }	
14	None		

Ad = adherence

Conty = continuity of layer

Cont = continuous

Examples 15 to 20

In these examples, the effects on the properties of the layer resulting from varying the zeolite concentration were studied; the dip time was 5 seconds, pH was 3.5, additive HPC, 1.6 g/litre.

Example No.	Zeolite Conc. g/l	Layer Thickness $\mu\text{m}$	Observation
15	0.1	---	not continuous
16	0.5	---	not continuous
17	0.8	1.0	continuous, few cracks
18	1.1	2.5	continuous, few cracks
19	1.6	5.0	continuous, cracks
20	2.1	6.5	continuous, cracks

Examples 21 to 26

In these Examples, the effect of the dipping time was studied; pH was 3.0, additive was HPC at 1.6 g/litre, zeolite content 1.1%.

Example No.	Dipping Time seconds	Layer Thickness $\mu\text{m}$	Observation
21	1	0.7 to 1.1	no cracks
22	3	1.5 to 2	no cracks
23	6	2	no cracks
24	10	2 to 3	no cracks
25	20	3.5	cracks
26	60	6.5 to 7	cracks

The experiments show that dipcoating can give good continuous layers of low thickness; reparation to remove cracks may be effected by multiple applications.

Example 27

This and the following example illustrate manufacture of a layer using hydrothermal crystallization techniques.

In this example, the ageing solution contained all the zeolite-forming ingredients.

A synthesis mixture was prepared from the following components, in parts by weight:

Colloidal ZSM-5 suspension, 50 nm mean particle size, 6.5% by weight ZSM-5	18.79
Tetrapropylammonium bromide (TPABr)	1.55
Ludox AS <sup>®</sup> 40 colloidal silica	6.25

Using the barrier-forming and spin-coating procedure of Example 1 a water-soaked alpha-alumina disk with 80 nm diameter pores is spincoated with part of the synthesis mixture. The coated disk is transferred to an autoclave and covered with the remainder of the synthesis mixture. The autoclave was transferred to an oven, heated to 160°C over the course of 2 hours, maintained at that temperature for 120 hours, and cooled to room temperature.

The cooled coated disk was washed in flowing tap water for 4 hours, washed twice in demineralized water and then twice more at 80°C. The disk was dried by heating in an oven at 10°C/hour to 110°C, maintained at 110°C for 5 hours, and allowed to cool at room temperature. Calcining was effected by heating at 10°C/hour to 550°C, maintaining at that temperature for 16 hours, and cooling at 60°C per hour to room temperature.

From optical and SEM observations - see Fig 6 - the resultant layer is about 1 µm thick and crack-free, with a final grain size of from 100 to 300 nm.

#### Example 28

In this example, the ageing solution contained only those ingredients not already in the layer.

A synthesis mixture was prepared from the following components, in parts by weight:

Colloidal silicalite 1 suspension, 20 to 30 nm particle size distributuion, 7.2 % by weight solids, including template present in the zeolite	20.00
Ludox AS <sup>®</sup> 40 colloidal silica	20.00
Demineralized water	22.50

An alpha-alumina disk was dipped into the solution for 5 seconds, and immediately placed in an autoclave and covered with an ageing solution, pH 11.5 with a molar composition of 6.36 (NH<sub>4</sub>)<sub>2</sub>O/1 TPABr/130 H<sub>2</sub>O/0.96 HNO<sub>3</sub>. The autoclave was put in an oven at 152°C and maintained there for 7 days. After removal from the autoclave, the disk was repeatedly washed with demineralized water at 70°C until the conductivity of the last wash - water was 10 microSiemens per centimetre. The disk was then dried at 40°C, relative humidity 60%, for several hours, followed by drying for 1 hour at 105°C.

Visual inspection showed the disk to be very homogeneous and smooth, with no visual terracing or scaling. By SEM it was seen that the layer had the crystal habit of silicalite - see Fig. 7 - with a mean diameter of 100 nm; the cross-section - Fig. 8 - indicating a layer thickness of about 10 µm.

#### Example 29

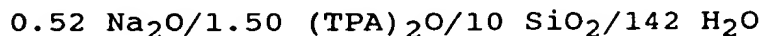
This example illustrates in situ formation of zeolite crystals on a support.

A synthesis solution was prepared from the following components, the parts being given by weight:

(20% by weight in water)	41.02
NaOH, pellets	0.58
SiO <sub>2</sub> powder (10% of water)	8.94

The sodium hydroxide was dissolved in the TPAOH solution at room temperature, the silica added, and the mixture heated to boiling with vigorous stirring until a clear solution was obtained. The solution was cooled,

weight loss compensated with demineralized water, and the solution filtered through a 0.45  $\mu\text{m}$  filter. The molar composition of the synthesis mixture was:



A quarter of an alpha-alumina disk, pore size 1  $\mu\text{m}$ , diameter 47 mm, was air dried for 2 hours at 150°C, and weighed. 25.05 g of synthesis solution was poured on to the disk in a 150 ml stainless steel autoclave. The autoclave was placed in an oven, heated up to 150°C in the course of 1 hour and maintained at that temperature for 24 hours.

After cooling the autoclave the support was removed, repeatedly washed with deionized water and air dried at 150°C for 2 hours. A disk weight increase of 6.9 % was noted.

The dried disk was then heated at 2°C/min to a temperature of 475°C and heated in air at that temperature for 6 hours. Comparison of SEMs of the original alpha-alumina surface - Fig. 9 - and of the calcined layer - Fig. 10 - shows that the surface of the disk is homogeneously coated with intergrown spherical crystals of about 0.4  $\mu\text{m}$  size, which show the typical crystal habit of silicalite.

#### Example 30

Example 29 was repeated except that crystallization took place at 98°C for 19 hours. An SEM - Fig. 11 - again shows a homogeneous coating of the disk surface, but the crystal size is now smaller, between 0.2 and 0.3  $\mu\text{m}$ .

#### Example 31

A synthesis solution was prepared as described in Example 29. The support was an alpha-alumina substrate with a pore size of 160 nm; this was dried at 185°C, placed on the bottom of a 300 ml stainless steel autoclave, covered with 220.4 g of synthesis solution, and the autoclave maintained at 120°C for 24 hours. After washing, drying and calcining at 475°C for 12 hours in air, the supported layer was examined by SEM. The photographs -

Figs. 12 to 14 show the surface, Fig. 15 shows a cross-section - indicate a uniform coating of  $0.3\text{ }\mu\text{m}$  intergrown silicalite crystals and a layer thickness of about  $0.5\text{ }\mu\text{m}$ .

#### Example 32

This example illustrates the manufacture of a zeolite layer by two in-situ crystallization steps at  $120^{\circ}\text{C}$ .

The support comprises a porous alpha-alumina disk, having an average pore diameter of  $160\text{ nm}$ , and polished on at least one side. After polishing the support is stored submerged in demineralized water until a day before the preparation of the zeolite layer. Then the support is placed in an oven, heated up at a rate of  $1^{\circ}\text{C}/\text{minute}$  to  $400^{\circ}\text{C}$ , kept at  $400^{\circ}\text{C}$  for 4 hours, and cooled down.

For the first crystallization step, a synthesis mixture is prepared by mixing silica (Baker,  $>99.75$  pure  $\text{SiO}_2$ ), Tetrapropyl-ammonium-hydroxide (TPAOH, Fluka practical grade, 20% in water), NaOH (Merck, 99.99 pure) and demineralized water to get 100 ml of mixture with the following molar composition:

$10\text{ SiO}_2 / 1.5\text{ (TPA)}_2\text{O} / 0.53\text{ Na}_2\text{O} / 142\text{ H}_2\text{O}$ .

The mixture is boiled on a hotplate for 5 minutes while stirring vigorously. Then the mixture is taken from the hotplate and left to cool down, after which  $\text{H}_2\text{O}$  is added to compensate for evaporation losses during boiling. The dry support disk is taken out of the oven and placed on the bottom of a stainless steel autoclave with the polished side facing up. The synthesis mixture is poured in the autoclave next to the disk, which is eventually submerged in the mixture. The autoclave is closed and placed in an oven at  $120^{\circ}\text{C}$  for 72 hours. After removal from the autoclave the disk is washed 5 to 10 times in demineralized water of  $70^{\circ}\text{C}$ .

For the second crystallization step, a fresh synthesis mixture, identical to the mixture described for the first step, is prepared. The disk is placed in a clean autoclave while still wet, in the same orientation as in the first step, and the fresh synthesis mixture is poured in the

autoclave so that the disk is completely submerged. The autoclave is closed and put in an oven at 120°C for 72 hours. After removal from the autoclave the disk is washed 5 to 10 times in demineralized water of 70°C. After washing the disk is dried in air at 30°C for 1.5 days. Then the disk is heated up in air at a rate of 10°C/hour to 550°C, kept at that temperature for 16 hours, and cooled down to room temperature at a rate of 20°C/hour.

X-Ray Diffraction (XRD) analysis shows that MFI-type zeolite crystals have formed on both the top and the bottom surfaces of the disk, the intensity of the XRD-peaks suggesting a zeolite layer thickness of a few microns. Scanning Electron Microscope (SEM) micrographs show that a dense layer, 3 to 5 micrometer in thickness, has formed at the top surface of the disk, and also at the bottom surface of the disk.

Examples 33, 34, 35 and 36

These examples illustrate the increase in the amount of zeolite formed on the support with increasing number of crystallization steps. The preparation is identical to that of Example 32, the number of crystallization steps varies from one to four.

XRD patterns have been obtained from these disks after drying but before the thermal treatment at 550°C. Comparison of the XRD-patterns shows that with each step the height of the MFI-zeolite peaks increases while the height of the alpha-alumina peaks decreases, as shown in the following table, where the intensity ratio refers to the ratio between the intensity of the MFI (501)(051)(431) peak and the alpha-alumina (012) peak:

example	number of steps	ratio
-----	-----	-----
33	1	0.37
34	2	0.71
35	3	1.41
36	4	2.78

This indicates that the amount of zeolite on the disk increases with each crystallization step.

#### Example 37

This example describes the Helium permeation characteristics of disks prepared using one or two crystallization steps similar to Example 32, the first crystallization step done at 120°C and the second crystallization step done at 90°C.

Helium permeation through the disk has been measured at total pressures in the range of 1 to 3 bar. Disks prepared using a single crystallization step at 120°C show He-permeations of several hundreds mmol/sm<sup>2</sup>bar, increasing with pressure. However, disks prepared using two crystallization steps (120°C and 90°C) show He-permeations of a few tens of mmol/sm<sup>2</sup>bar that are constant over the pressure range of 1-3 bar.

#### Example 38

A membrane fabricated according to the process of example 32 was mounted into a holder and a 'Wicke-Kallenbach' experiment was carried out. A gas mixture of 49.9% n-butane, 49.9% methane and 0.2% i-butane was passed over one side of the membrane, the other side being continuously purged with a dry helium stream. Both sides of the membrane were kept at atmospheric pressure. The analyses of both gas streams by an on-line gas chromatograph were evaluated and transformed to the corresponding fluxes through the membrane. Selectivities are given by:

$$S = (C_1(\text{perm})/C_1(\text{ret})) / (C_2(\text{perm})/C_2(\text{ret}))$$
, where  $C_1$  and  $C_2$  are concentrations of components 1 and 2, and permeate and retentate streams are indicated by perm and ret, respectively. The calculated fluxes and selectivities are given in the following table:

T [C]	Methane flux [mol/m <sup>2</sup> s] *10 <sup>4</sup>	n-Butane flux [mol/m <sup>2</sup> s] *10 <sup>3</sup>	S (n-butane/ methane)
25	1.35	2.44	18.07
50	2.15	2.67	12.42
75	2.78	2.81	10.11
100	4.94	3.14	6.36
125	8.75	3.36	3.84
150	13.1	3.40	2.60
175	17.1	3.24	1.89
200	21.3	3.07	1.44

(Reference:

E. Wicke and R. Kallenbach, Surface diffusion of carbon dioxide in activated charcoals, Kolloid Z., 97 (1941), 135)

#### Example 39

A membrane fabricated according to the process of example 32 was used for a test similar to that in example 38. A gas mixture of 48.3% methane and 51.7% i-butane was used as feed stream. The calculated fluxes and selectivities are given in the following table:

T [C]	Methane flux [mol/m <sup>2</sup> s] *10 <sup>4</sup>	i-Butane flux [mol/m <sup>2</sup> s] *10 <sup>5</sup>	S (methane/ i-butane)
25	1.29	7.18	1.92
50	2.38	7.29	3.49
75	3.76	7.41	5.43
100	4.90	9.38	5.59
125	6.29	13.2	5.10
150	8.42	17.7	5.09
175	12.2	22.3	5.86
200	17.8	25.7	7.41

#### Example 40

A membrane fabricated according to the process described in example 32 was used for a test similar to that in example 38. A gas mixture of 50.0% n-butane and 50.0% i-butane was

used as feed stream. The calculated fluxes and selectivities are given in the following table:

T [C]	n-Butane flux [mol/m <sup>2</sup> s] *10 <sup>3</sup>	i-Butane flux [mol/m <sup>2</sup> s] *10 <sup>4</sup>	S (n-butane/ i-butane)
25	1.33	0.26	51.95
50	1.66	0.71	23.55
75	1.99	0.82	24.21
100	2.29	1.21	18.93
125	2.24	1.60	14.00
150	2.45	1.85	13.24
175	2.28	1.89	12.06
200	2.26	2.06	10.97

#### Example 41

A membrane fabricated according the description in example 32 was used for a test similar to that in example 38. A gas mixture containing 0.31% p-xylene, 0.26% o-xylene and methane as balance was used as feed stream. The calculated fluxes and selectivities are given in the following table:

T [C]	p-Xylene flux [mol/m <sup>2</sup> s] *10 <sup>6</sup>	o-Xylene flux [mol/m <sup>2</sup> s] *10 <sup>7</sup>	S (p-xylene/ o-xylene)
100	3.54	0.49	60.10
150	3.43	0.66	43.46
175	3.33	0.92	30.49
200	3.02	1.22	20.76

#### Example 42

A membrane fabricated according the description in example 32 was used for a test similar to that in example 38. A gas mixture containing 5.5% benzene, 5.5% cyclohexane and methane as balance was used as feed stream. The calculated fluxes and selectivities are given in the following table:

T [C]	Benzene flux [mol/m <sup>2</sup> s] *10 <sup>7</sup>	Cyclohexane flux [mol/m <sup>2</sup> s] *10 <sup>7</sup>	S (benzene/ cyclohexane)
25	2.64	0.53	5.01
50	3.03	0.66	4.60
75	4.61	0.92	4.99
100	5.67	1.98	2.86
125	9.23	3.20	2.88
150	9.49	4.48	2.12
175	10.9	3.30	3.30
200	17.8	4.48	3.97

Example 43

A membrane fabricated according the description in example 32 was used for a test similar to that in example 38. A gas mixture containing 7.6% n-hexane, 15.4% 2,2-dimethylbutane and methane as balance was used as feed stream. The calculated fluxes and selectivities are given in the following table:

T [C]	n-Hexane flux [mol/m <sup>2</sup> s] *10 <sup>4</sup>	2,2-Dimethylbutane flux [mol/m <sup>2</sup> s] *10 <sup>7</sup>	S (benzene/ cyclohexane)
20	1.2	1.9	600
50	1.5	2.3	640
100	3.1	2.7	1150
150	3.0	1.9	1560
200	2.4	1.2	2090

Example 44

This example illustrates the growth of zeolite layers by multiple crystallizations, without refreshing the synthesis mixture as in example 32, but by increasing the crystallization temperature stepwise.

A porous alpha-alumina disk with a pore diameter of 160 nm and polished on one side was cut into four equal-sized parts. The parts were weighed and placed, polished side up, on teflon rings resting on the bottom of a stainless steel autoclave. In the autoclave was poured 70.22 g of a synthesis solution with a molar composition of

10 SiO<sub>2</sub> / 1.56 (TPA)<sub>2</sub>O / 0.275 Na<sub>2</sub>O / 147 H<sub>2</sub>O.

The open autoclave was placed in an exsiccator, which was then evacuated during 0.5 hours to increase the penetration of synthesis solution into the disks. Then the autoclave was taken out of the exsiccator, closed, and placed in an oven at room temperature. The oven was heated up to 90°C in a few minutes and kept at that temperature for 48 hours. The autoclave was then cooled to room temperature, opened and one of the support pieces was removed. The autoclave was closed again and placed in an oven at room temperature. The oven was heated up to 110°C in a few minutes and kept at that temperature for 24 hours. The autoclave was cooled down again and the second piece was removed. The temperature cycle was repeated two more times, first for 24 hours at 130°C and then for 24 hours at 150°C. The four pieces of the disk were all washed with demineralized water of 70°C until the washing water had a conductivity of about 6 micro Siemens/cm, dried at 105°C and cooled to room temperature in an exsiccator. It was observed that with each aging step the weight of the disk pieces increased, as shown in the following table:

disk piece #	temperature history 'C	weight increase %
-----	-----	-----
1	90	0.88
2	90 + 110	2.04
3	90 + 110 + 130	3.50
4	90 + 110 + 130 + 150	5.63

XRD analysis showed that with each ageing step the intensity of the zeolite peaks increased with respect to the intensity of the alpha-alumina peaks, as shown in the following table:

peak intensity ratio:	
disk piece #	peak at d=0.385nm (MFI) / peak at d=0.348nm (Al <sub>2</sub> O <sub>3</sub> )
-----	-----
1	0.190
2	0.217
3	0.236
4	0.332

These results indicate that with each ageing step at a higher temperature new zeolite crystals are deposited on the support.

CLAIMS

1. A supported inorganic layer comprising contiguous particles of a crystalline molecular sieve, the particles having a mean particle size within the range of from 20 nm to 1  $\mu$ m.

2. A supported inorganic layer comprising particles of a crystalline molecular sieve, the particles having a mean particle size within the range of from 20 to 200 nm.

3. A process for the manufacture of a layer by deposition on a support from a colloidal zeolite suspension obtainable by preparing an aqueous synthesis mixture comprising a source of silica and an organic structure directing agent in a proportion sufficient to effect substantially completed solution of the silica source in the mixture at the boiling temperature of the mixture, and crystallization from the synthesis mixture.

4. A process as claimed in claim 3, wherein after its deposition on the support the supported zeolite layer is activated.

5. A process for the manufacture of a layer comprising a crystalline molecular sieve on a porous support, which comprises pre-treating the porous support to form at a surface thereof a barrier layer, and applying to the support a reaction mixture comprising a colloidal suspension of molecular sieve crystals, having a mean particle size of at most 100 nm, colloidal silica and optionally an organic structure directing agent, and if desired or required activating the resulting molecular sieve layer.

6. A process as claimed in claim 4, wherein the barrier is a temporary barrier, and is advantageously water.

7. A process as claimed in claim 4, wherein the barrier is a permanent barrier of smaller pore size than the support.

8. A process for the manufacture of a layer comprising a crystalline molecular sieve on a porous

support which comprises applying to the support by dip-coating a colloidal suspension of molecular sieve crystals having a mean particle size of at most 100 nm, drying the resulting gel on the support and if desired or required activating the resulting layer.

9. A process for the manufacture of a layer comprising a crystalline molecular sieve on a porous support, which comprises applying to or forming on the support a layer comprising amorphous silica containing seeds of a zeolite having a mean particle size of at most 100 nm, subjecting the layer to hydrothermal crystallization, and if desired or required calcining the crystallized layer.

10. A process for the manufacture of a layer comprising a crystalline molecular sieve on a porous support, which comprises preparing a synthesis mixture comprising a source of silica and an organic structure directing agent in a proportion sufficient to effect substantially complete dissolution of the silica source in the mixture at the boiling temperature of the mixture, immersing the support in the synthesis mixture, crystallizing zeolite from the synthesis mixture onto the support, and if desired or required activating the crystallized layer.

11. The layer produced by the process of anyone of claims 3 to 10 or by any combination of such processes.

12. A layer as claimed in claim 1 or claim 11, wherein the particle size of the molecular sieve crystals in the layer is within the range of from 20 to 500 nm, advantageously from 20 to 300 nm.

13. A layer as claimed in any one of claims 1, 2, 11 and 12, wherein the particle size distribution is such that at least 95% of the particles have a size within  $\pm 33\%$  of the mean, advantageously  $\pm 10\%$  of the mean, and preferably  $\pm 7.5\%$  of the mean.

14. A layer as claimed in any one of claims 1, 2 and 11 to 13, wherein the layer thickness is within

the range of from 0.1 to 20  $\mu\text{m}$ , advantageously 0.1 to 15  $\mu\text{m}$ , advantageously 0.1 to 2  $\mu\text{m}$ .

15. A layer as claimed in any one of claims 1, 2, and 11 to 14, wherein the layer primarily contains nanopores i.e., pores between 1 and 10 nm.

16. A layer as claimed in any one of claims 1, 2 and 11 to 14, wherein the layer primarily contains micropores, i.e., pores between 0.2 and 1 nm.

17. A layer as claimed in any one of claims 1, 2, and 11 to 14, wherein the layer comprises molecular sieve crystals in a particulate matrix, the pore structure being defined by the interstices between the particles, between the crystals, and between the particles and the crystals, the pore structure advantageously being between 0.2 and 1 nm in size.

18. A layer as claimed in any one of claims 1, 2, and 11 to 17, wherein the molecular sieve is a zeolite.

19. A process for the separation of a fluid mixture which comprises contacting the mixture with one face of a layer as claimed in any one of claims 1, 2 and 11 to 18 under conditions such that at least one component of the mixture has a different steady state permeability through the layer from that of another component and recovering a component or mixture of components from the other face of the layer.

20. A process for catalysing a chemical reaction which comprises contacting a feedstock with a layer as claimed in any one of claims 1, 2, and 11 to 18, which is in active catalytic form under catalytic conversion conditions and recovering a composition comprising at least one conversion product.

21. A process for catalysing a chemical reaction which comprises contacting a feedstock with one face of a layer as claimed in any one of claims 1, 2, and 11 to 18, that is in the form of a membrane and in active catalytic form, under catalytic conversion conditions, and recovering from an opposite face of the layer at least one

conversion product, advantageously in a concentration differing from its equilibrium concentration in the reaction mixture.

FIG.1

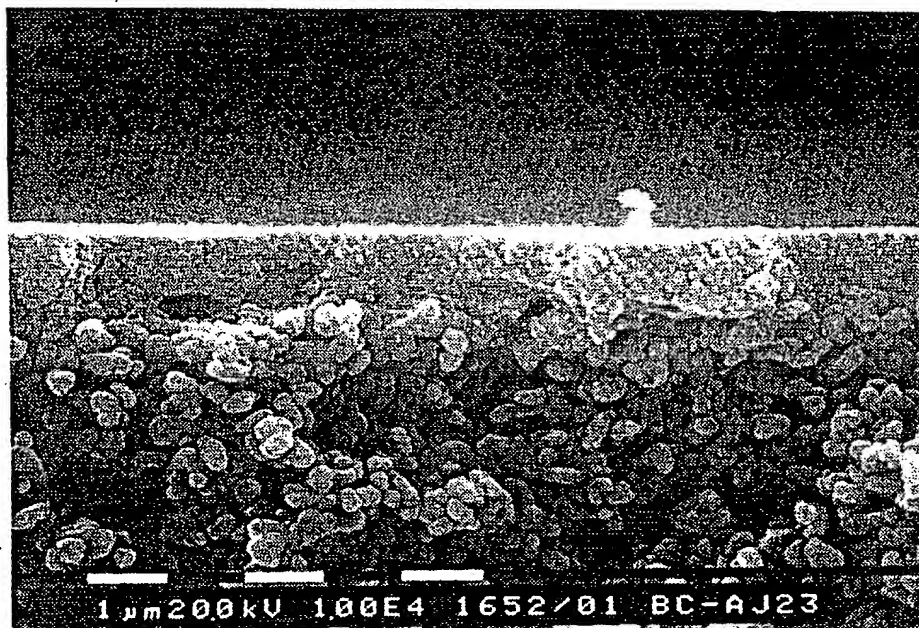
SILICA/  
ZEOLITE  
LAYER1  $\mu\text{m}$  $\alpha$  ALUMINA  
SUBSTRATE

FIG.2

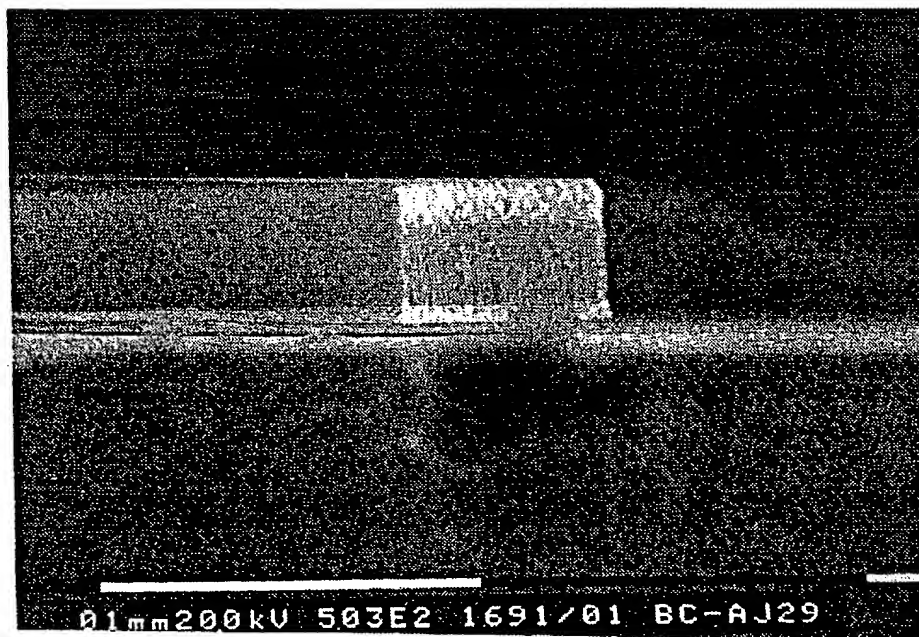
SILICA/  
ZEOLITE  
LAYER  
40  $\mu\text{m}$  $\alpha$  ALUMINA  
SUBSTRATE

FIG. 3

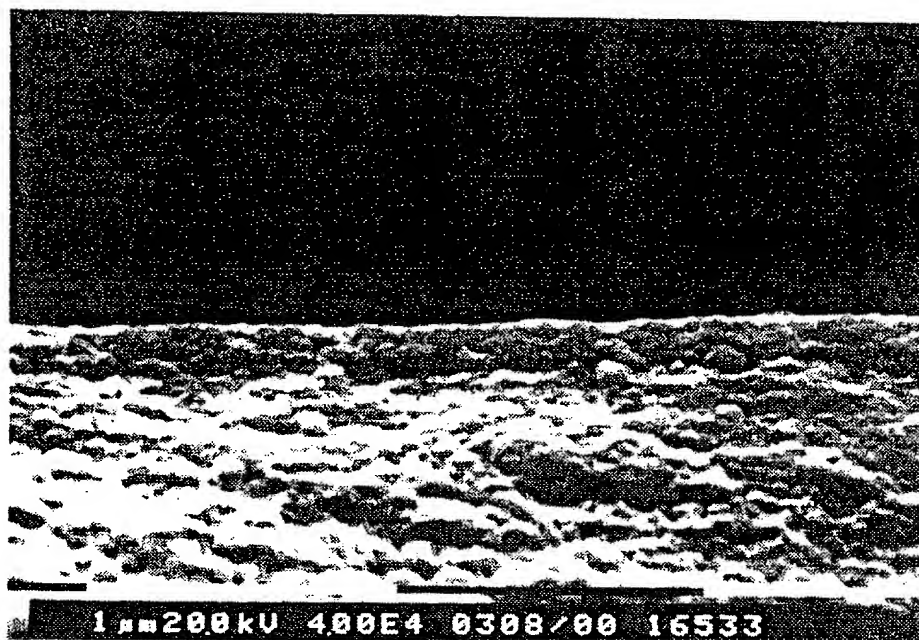
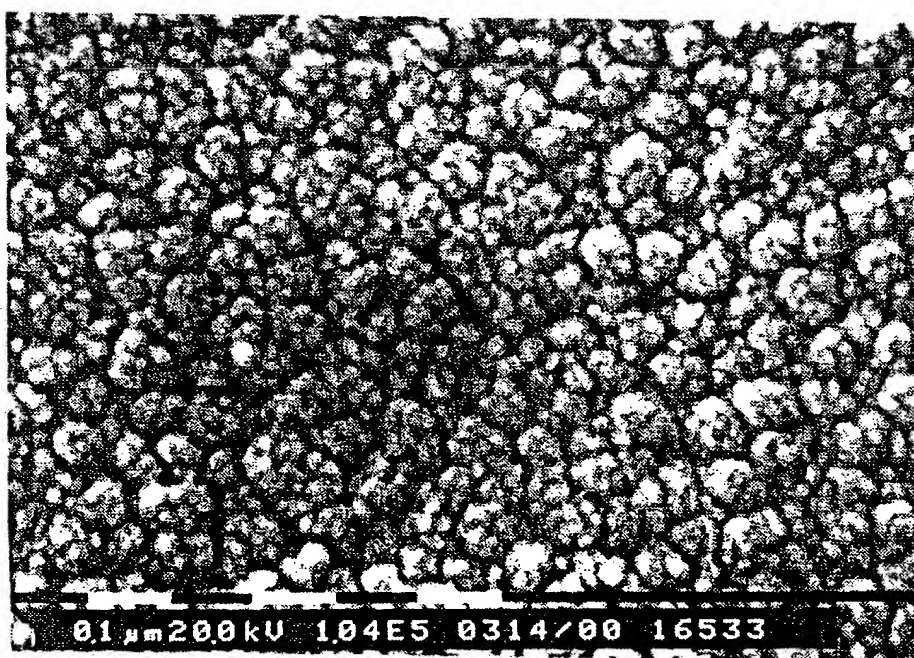
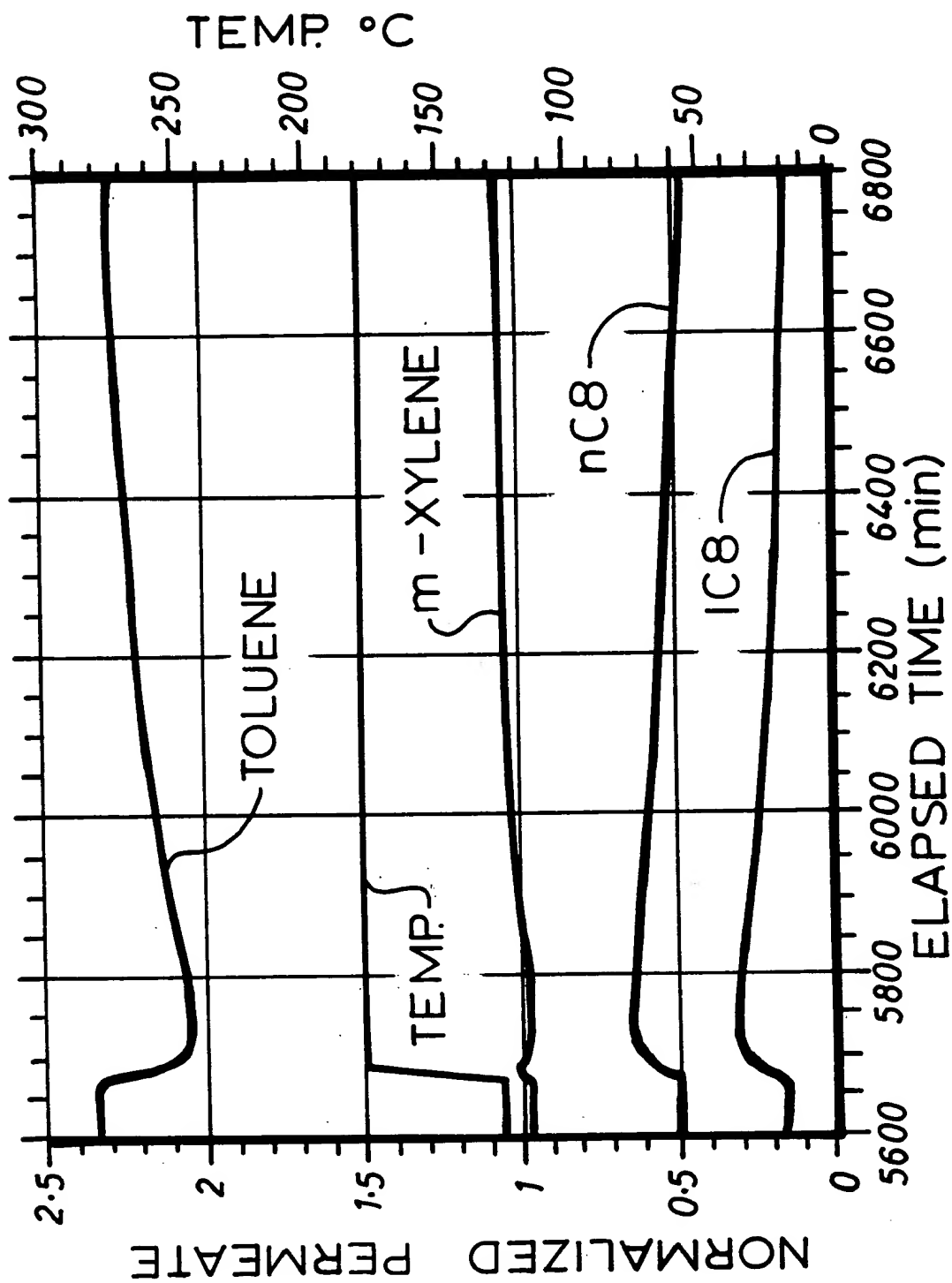


FIG. 4



**FIG.5**  
ZSM-5/SILICA-ALUMINA MEMBRANE



4/9

FIG. 6

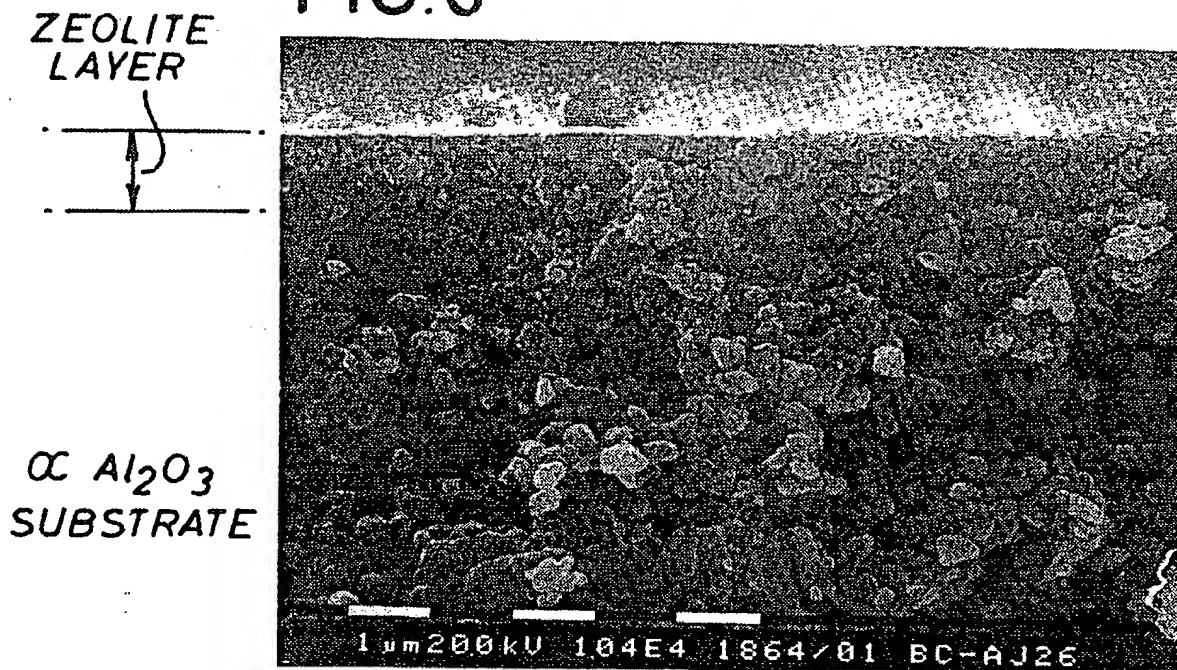


FIG. 7

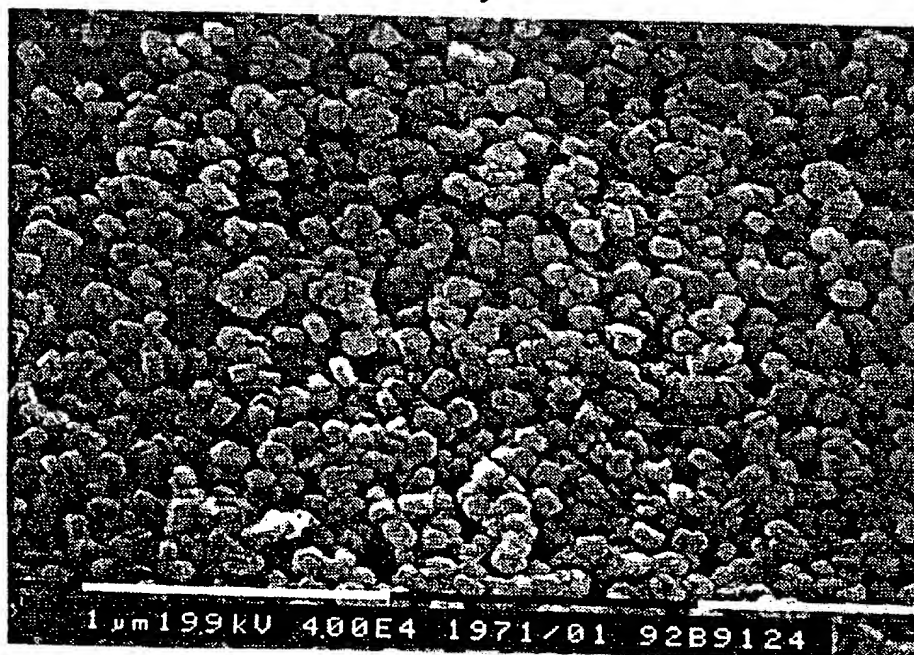
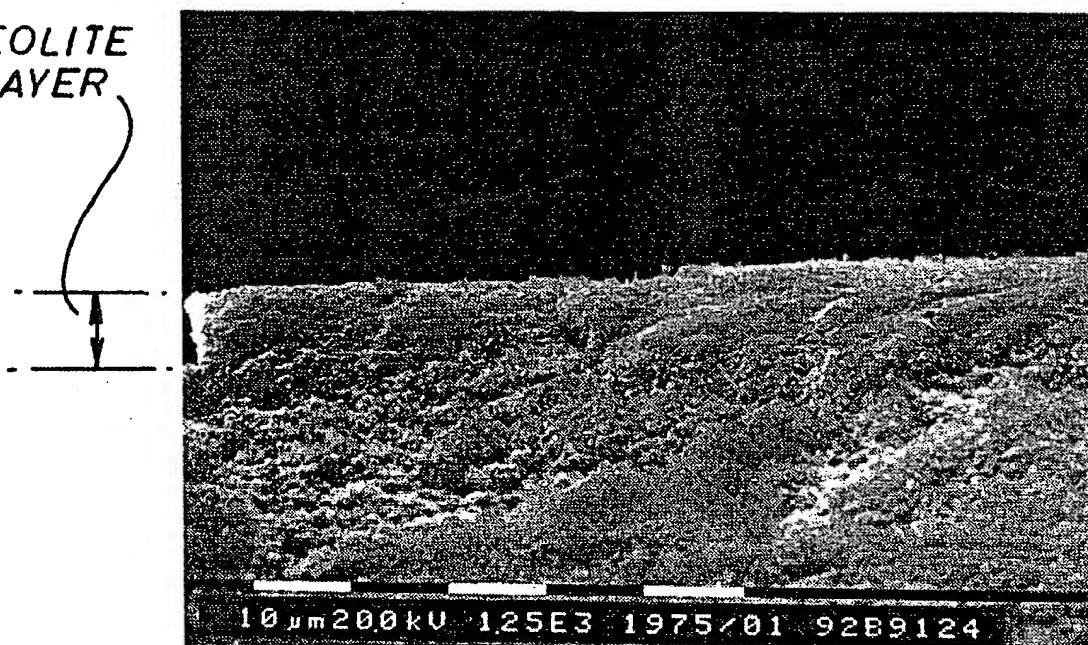
 $\times 40,000$ 

FIG. 8

ZEOLITE  
LAYER



$\alpha$ -Al<sub>2</sub>O<sub>3</sub>  
SUBSTRATE

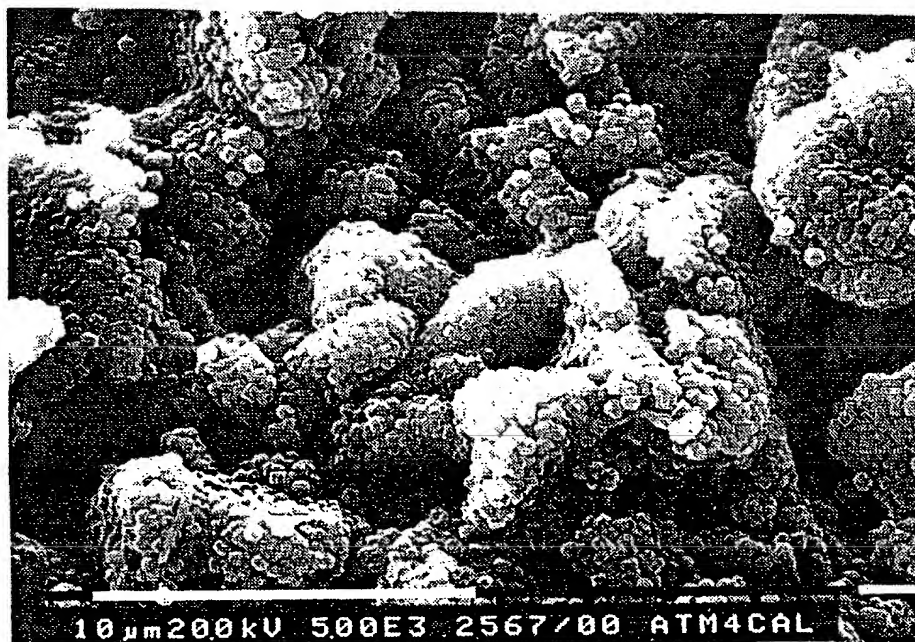
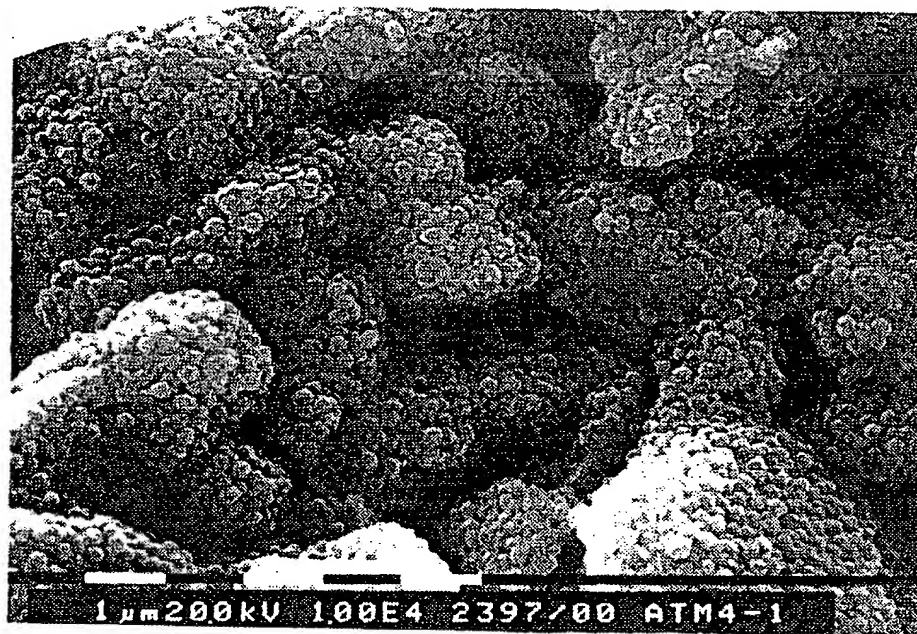
**FIG. 9** *x 5,000***FIG. 10** *x 5,000*

FIG.11  $\times 10,000$ FIG.12  $\times 156$ 

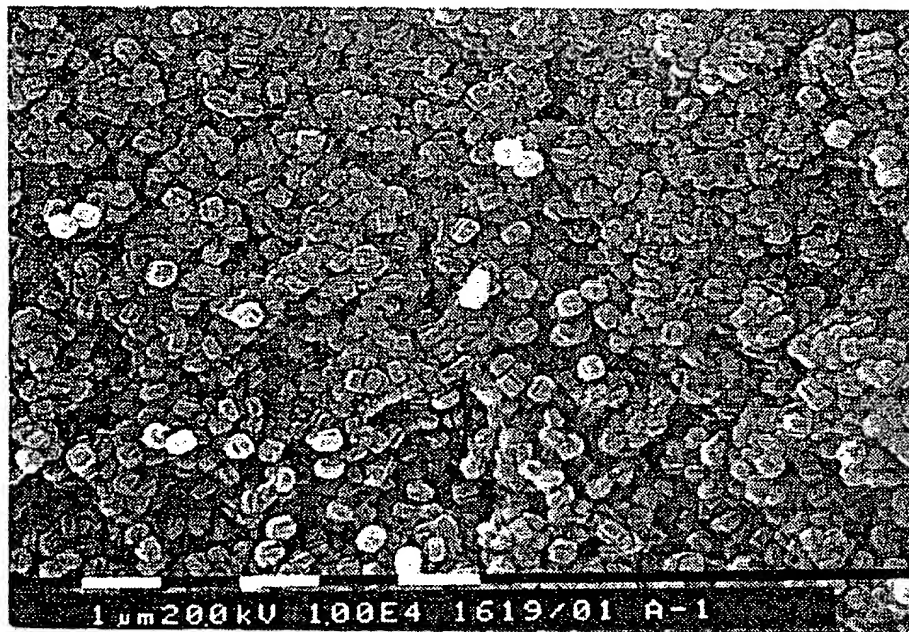
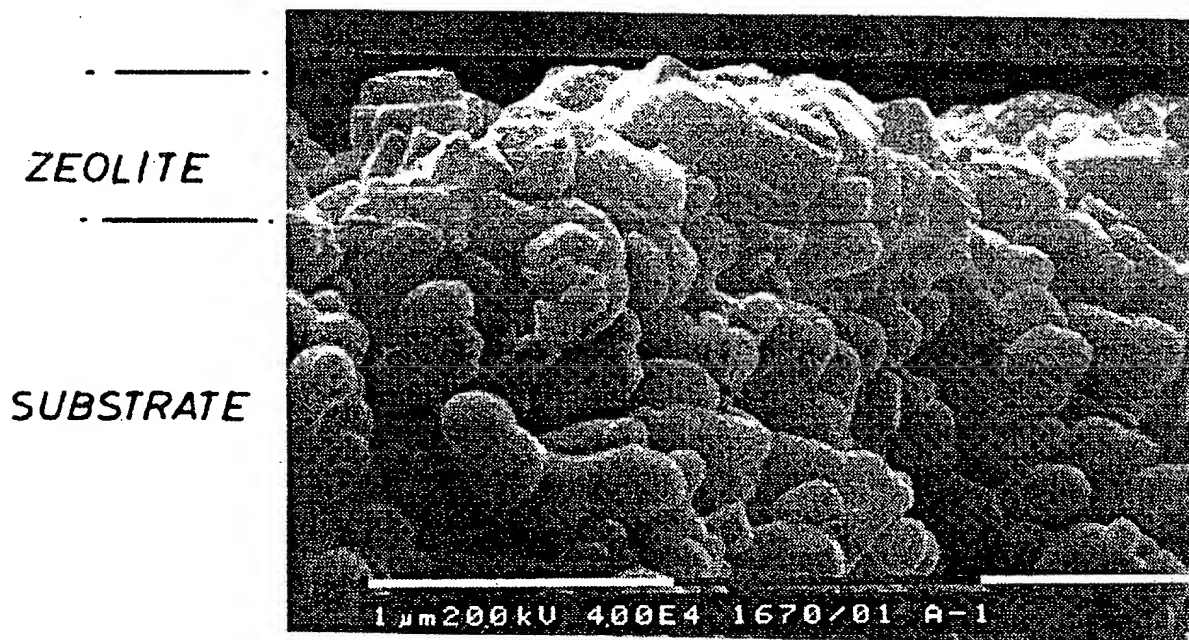
**FIG.13**  $\times 10,000$ **FIG.14**  $\times 80,000$ 

FIG.15



## INTERNATIONAL SEARCH REPORT

Inter. Application No

PCT/EP 94/01301

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 B01J20/18 B01D71/02 C01B33/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 B01J B01D C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 135 069 (SUZUKI HIROSHI) 27 March 1985 cited in the application see page 4, line 7 - page 27, line 6 ---	1,3
A	EP,A,0 481 660 (THE BRITISH PETROLEUM COMPANY P.L.C.) 22 April 1992 cited in the application see page 3, line 14 - page 5, line 11 ---	1,3
A	EP,A,0 397 216 (ALCAN INTERNATIONAL LIMITED) 14 November 1990 cited in the application see page 2, line 39 - page 3, line 23 ---	1,3
A	EP,A,0 149 343 (EXXON RESEARCH AND ENGINEERING COMPANY) 24 July 1985 see claim 1 --- -/--	3

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Date of the actual completion of the international search

17 August 1994

Date of mailing of the international search report

31. 08. 94

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 511 739 (NGK INSULATORS LTD) 4 November 1992 see page 4, line 22 - line 34 ---	3
A	US,A,5 019 263 (HAAG ET AL) 28 May 1991 see column 9, line 22 - column 10, line 39 ---	1,3
A	JOURNAL OF MEMBRANE SCIENCE, vol.73, 1992 pages 119 - 128 MENG-DONG JIA ET AL cited in the application see page 120, left column, line 32 - page 121, left column, line 5 -----	1,3

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Application No

PCT/EP 94/01301

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## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>93A007</b>	<b>FOR FURTHER ACTION</b>	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. <b>PCT/EP 94/01301</b>	International filing date (day/month/year) <b>25/04/94</b>	(Earliest) Priority Date (day/month/year) <b>23/04/93</b>
Applicant <b>EXXON CHEMICAL PATENTS INC. et al.</b>		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ Certain claims were found unsearchable (see Box I).
2. ☐ Unity of invention is lacking (see Box II).
3. ☐ The international application contains disclosure of a nucleotide and/or amino acid sequence listing and the international search was carried out on the basis of the sequence listing
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  - ☐ furnished by the applicant separately from the international application,
    - ☐ but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
  - ☐ Transcribed by this Authority
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  - ☐ the text has been established by this Authority to read as follows:
5. With regard to the abstract,
  - ☒ the text is approved as submitted by the applicant.
  - ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.
6. The figure of the drawings to be published with the abstract is:  
Figure No. \_\_\_\_\_
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  - ☐ because this figure better characterizes the invention.

☒ None of the figures.

## A. CLASSIFICATION OF SUBJECT MATTER

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Fax: (+ 31-70) 340-3016

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Clement, J-P

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A	US,A,5 019 263 (HAAG ET AL) 28 May 1991 see column 9, line 22 - column 10, line 39 ---	1,3
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 94/01301

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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